REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 37 | 2020

# Interlaboratory Proficiency Test 05/2020

## Metals in natural waters

**Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas**

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## ABSTRACT

**Interlaboratory Proficiency Test 05/2020**

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in natural waters in April-April–May 2020. The measurands for the synthetic, ground water and lake water samples were: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V, and Zn. In total 16 participants joined in the PT. In this proficiency test 88 % of the results were satisfactory when deviation of 10–30 % from the assigned value was accepted.

Basically, either the metrologically traceable concentration, the calculated concentration or the robust mean, the mean or the median of the results reported by the participants was used as the assigned value for the measurands. The evaluation of the performance of the participants was carried out using z scores.

Warm thanks to all the participants in this proficiency test!

**Keywords:** water analysis, metals, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V, Zn, water, environmental laboratories, proficiency test, interlaboratory comparisons

## TIIVISTELMÄ

**Laboratorioiden välinen pätevyyskoe 05/2020**

Proftest SYKE järjesti pätevyyskokeen ympäristönäytteitä analysoiville laboratorioille huhti–toukokuussa 2020. Pätevyyskokeessa määritettiin Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V ja Zn synteettisestä näytteestä sekä pohja- ja järvivesinäytteistä. Pätevyyskokeeseen osallistui yhteensä 16 osallistujaa. Koko tulosaineistossa hyväksyttäviä tuloksia oli 88 %, kun vertailuarvosta sallittiin 10–30 %:n poikkeama.

Testisuureen vertailuarvona käytettiin joko metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta tai osallistujien ilmoittamien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla.

Kiitos pätevyyskokeen osallistujille!

**Avainsanat:** vesianalyysi, metallit, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V, Zn, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

## SAMMANDRAG

**Provningsjämförelse 05/2020**

Proftest SYKE genomförde en provningsjämförelse i april–maj 2020, som omfattade bestämningen av Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V och Zn i syntetisk provet och natur- och grundvattenproverna. Tillsammans 16 laboratorier deltog i jämförelsen. I jämförelsen var 88 % av alla resultaten tillfredsställande, när avvikelsen 10–30 % från referensvärdet accepterades.

Som referensvärde av analytens koncentration användes mest det metrologiska spårbara värdet, teoretiska värdet eller robust medelvärdet, medelvärdet eller median av deltagarnas resultat. Resultaten värderades med hjälp av z-värden.

Ett varmt tack till alla deltagarna i testet!

**Nyckelord:** vattenanalyser, metaller, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V, Zn, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

# 1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of metals in natural waters in April–May 2020. The measurands for the synthetic sample and natural and ground water samples were: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V, and Zn. In total 16 participants joined in the PT. In the PT the results of Finnish participants providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test has been carried out in accordance with the international standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest SYKE.

# 2 Organizing the proficiency test

## 2.1 Responsibilities

**Organizer**

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Mustialankatu 3, FI-00790 Helsinki, Finland
Phone: +358 295 251 000, Email: proftest@environment.fi

**The responsibilities in organizing the proficiency test**

| | |
|---|---|
| Mirja Leivuori | coordinator |
| Riitta Koivikko | substitute for coordinator |
| Keijo Tervonen | technical assistance |
| Markku Ilmakunnas | technical assistance |
| Sari Lanteri | technical assistance |
| Ritva Väisänen | technical assistance |

**Analytical experts**

| | |
|---|---|
| Teemu Näykki | Hg, ID-ICP-MS (SYKE) |
| Timo Sara-Aho | other measurands, ID-ICP-MS (SYKE) |

## 2.2 Participants

In total 16 participants joined in this proficiency test, 14 from Finland and 2 from abroad (Appendix 1). Almost 88 % of the participants used accredited analytical methods at least for a part of the measurands. For this proficiency test, the organizing laboratory has the code 7 (SYKE, Helsinki, T003, ISO/IEC 17025, www.finas.fi/sites/en) in the result tables.

## 2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic sample and natural and ground water samples. The sample preparation is described in details in the Appendix 2.

The synthetic sample A1M was prepared from the NIST traceable commercial reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The sample N2M was lake water collected from the Lake Bodomjärvi, located in southern Finland and the sample G3M was ground water collected from the southern Finland. To these samples additions of single element standard solutions (Merck CertiPUR®) were done when needed (Appendix 2). The water samples were acidified with nitric acid with the exception of samples for mercury, which were acidified with the hydrochloric acid.

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by analyzing Cd, Cu, Hg, and Zn. According to the test results all used vessels fulfilled the purity requirements.

The delivered samples included synthetic sample and natural as well as ground water samples. The samples were delivered on 21 April 2020 to the participants. The samples arrived to the participants mainly on 22 April 2020.

The samples were requested to be measured as follows:

- Hg latest on 30 April 2020
- Other samples latest on 8 May 2020

The results were requested to be reported at the latest on 8 May 2020. Most of the participants delivered the results accordingly and two participants delivered the results on 11 May 2020. The preliminary results were delivered to the participants via ProftestWEB and email on 20 May 2020.

## 2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing Cd, Cr, Hg, Pb, Se, and Zn. More detailed information of the homogeneity studies is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials. However, homogeneity of these was checked by parallel measurements of three samples.

Based on the earlier similar proficiency tests the water samples are known to be stable over the given time period for the test.

## 2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with some clarification for their performance in the PT. All the feedback is valuable and is exploited when improving the activities.

## 2.6 Processing the data

### 2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result was reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [4].

### 2.6.2 Assigned values

For the synthetic sample A1M the NIST traceable calculated values were used as the assigned values, with the exception of B, Hg and Pb. The assigned values for Hg and Pb are based on the results of the metrologically traceable isotope dilution (ID) ICP-MS technique for the samples A1M, A1Hg, N2M, N2Hg, G3M, and G3Hg. The assigned value based on the ID-ICP-MS method is the mean of the homogeneity results and the test result (9 or 12 results). The ID-ICP-MS method is accredited for soluble lead and mercury in synthetic sample and natural as well as waste waters in the scope of calibration laboratory (K054; www.finas.fi/sites/en). For the other samples and measurands the consensus value of the reported results was used as the assigned value. The robust mean of the reported results was used as the assigned value for Cu (in G3M), Fe (in N2M and G3M), and Mn (in N2M and G3M). When the number of results was low ($n_{stat}$ <12), the mean or the median of the reported results was used as the assigned value (Appendix 5).

The robust mean, the mean or the median of the participant results is not metrologically traceable assigned value. As it was not possible to have metrologically traceable assigned value, the robust mean, the mean or the median of the reported results was the best available value to be used as the assigned value. The reliability of the assigned value was statistically tested [2, 3].

For the calculated assigned values, the expanded uncertainty ($k=2$) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

When the robust mean, the mean or the median of the participant results was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation, respectively [2, 4]. For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method.

The uncertainties of the calculated and the metrologically traceable assigned values for metals in the synthetic samples varied between 0.5 and 3 %. When using the robust mean, the mean or the median of the participant results as the assigned value, the uncertainties of the assigned values varied between 1.4 and 7.2 % (Appendix 5).

**The assigned values have not been changed after reporting the preliminary results.**

### 2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated with the z scores. The standard deviation for proficiency assessment was estimated based on the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2\times s_{pt}$, at the 95 % confidence level) was set to 10–30 % depending on the measurand and the sample.

**The standard deviations for the proficiency assessment have not been changed after reporting the preliminary results.**

When using the robust mean, the mean or the median as the assigned value, its reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where $u_{pt}$ is the standard uncertainty of the assigned value and $s_{pt}$ is the standard deviation for proficiency assessment [3]. When testing the reliability of the assigned value the criterion was fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the standard deviation for proficiency assessment ($s_{pt}$) with the robust standard deviation ($s_{rob}$) or the standard deviation (s, $n_{stat}<12$) of the reported results (the criterion) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was fulfilled.

# 3 Results and conclusions

## 3.1 Results

The summary of the results of the proficiency test is shown in Table 1. The terms used in the results tables are presented in Appendix 6. The results and the performance of each participant are presented in Appendix 7. The summary of the z scores is shown in Appendix 8. In Appendix 9 the z scores are shown in the ascending order. The reported results with their expanded uncertainties ($k$=2) and grouped according to the used methods are presented in Appendix 10.

The robust standard deviations of the results varied mainly from 2.1 % to 24 % (Table 1). The robust standard deviation of results was lower than 10 % for 87 % of the results and lower than 20 % for 98 % of the results (Table 1). The highest standard deviation (24.4 %) was for B in the ground water G3M sample (Table 1). The robust standard deviations for water samples were approximately on the same level than in the previous similar proficiency test MET 04/2019 [5], where the robust standard deviations varied from 0.6 % to 22 % for the water samples.

Table 1. The summary of the results in the proficiency test 05/2020.

| Measurand | Sample | Unit | Assigned value | Mean | Rob. mean | Median | $s_{rob}$ | $s_{rob}$ % | 2 x $s_{pt}$ % | $n_{all}$ | Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | A1M | µg/l | 112 | 113 | 113 | 113 | 7 | 6.2 | 10 | 12 | 92 |
| | G3M | µg/l | 91.7 | 91.7 | 90.9 | 91.1 | 6.1 | 6.7 | 15 | 13 | 85 |
| | N2M | µg/l | 409 | 409 | 409 | 415 | 23 | 5.7 | 15 | 14 | 93 |
| As | A1M | µg/l | 7.25 | 6.95 | 6.95 | 6.94 | 0.22 | 3.2 | 10 | 10 | 100 |
| | G3M | µg/l | 5.17 | 5.17 | 5.17 | 5.20 | 0.14 | 2.6 | 10 | 11 | 91 |
| | N2M | µg/l | 0.57 | 0.57 | 0.57 | 0.58 | 0.02 | 2.8 | 10 | 11 | 91 |
| B | A1M | µg/l | 18.3 | 18.2 | 17.6 | 18.3 | 2.7 | 15.6 | 25 | 10 | 78 |
| | G3M | µg/l | 38.9 | 38.9 | 35.0 | 38.9 | 8.5 | 24.4 | 25 | 10 | 67 |
| | N2M | µg/l | 28.4 | 28.2 | 27.4 | 28.4 | 3.3 | 12.1 | 25 | 11 | 60 |
| Ba | A1M | µg/l | 9.50 | 9.21 | 9.21 | 9.20 | 0.36 | 3.9 | 10 | 11 | 100 |
| | G3M | µg/l | 8.44 | 8.44 | 8.44 | 8.37 | 0.30 | 3.6 | 15 | 11 | 91 |
| | N2M | µg/l | 26.5 | 26.5 | 26.5 | 26.1 | 1.0 | 3.8 | 10 | 12 | 92 |
| Cd | A1M | µg/l | 0.33 | 0.32 | 0.33 | 0.32 | 0.01 | 4.6 | 15 | 11 | 90 |
| | G3M | µg/l | 0.33 | 0.32 | 0.33 | 0.33 | 0.02 | 7.6 | 15 | 11 | 82 |
| | N2M | µg/l | 0.51 | 0.51 | 0.51 | 0.51 | 0.02 | 4.7 | 15 | 12 | 82 |
| Co | A1M | µg/l | 1.35 | 1.31 | 1.31 | 1.31 | 0.06 | 4.6 | 10 | 10 | 100 |
| | G3M | µg/l | 2.04 | 2.04 | 2.04 | 2.00 | 0.10 | 5.2 | 15 | 10 | 90 |
| | N2M | µg/l | 1.06 | 1.05 | 1.05 | 1.06 | 0.06 | 5.3 | 15 | 11 | 82 |
| Cr | A1M | µg/l | 2.35 | 2.35 | 2.35 | 2.36 | 0.08 | 3.5 | 15 | 11 | 100 |
| | G3M | µg/l | 3.12 | 3.12 | 3.12 | 3.11 | 0.11 | 3.4 | 15 | 11 | 91 |
| | N2M | µg/l | 1.46 | 1.46 | 1.46 | 1.46 | 0.05 | 3.3 | 15 | 12 | 92 |
| Cu | A1M | µg/l | 21.5 | 21.4 | 21.3 | 21.2 | 0.8 | 3.7 | 10 | 12 | 92 |
| | G3M | µg/l | 24.9 | 24.9 | 24.9 | 25.1 | 1.2 | 4.7 | 15 | 13 | 92 |
| | N2M | µg/l | 6.00 | 5.98 | 5.96 | 6.00 | 0.18 | 3.0 | 15 | 13 | 92 |
| Fe | A1M | µg/l | 77.5 | 75.1 | 75.5 | 74.7 | 4.6 | 6.0 | 10 | 12 | 92 |
| | G3M | µg/l | 66.4 | 66.4 | 66.4 | 66.9 | 3.8 | 5.7 | 15 | 14 | 71 |
| | N2M | µg/l | 247 | 247 | 247 | 248 | 9 | 3.6 | 10 | 15 | 93 |

Table 1. The summary of the results in the proficiency test 05/2020.

| Measurand | Sample | Unit | Assigned value | Mean | Rob. mean | Median | $s_{rob}$ | $s_{rob}$ % | 2 x $s_{pt}$ % | $n_{all}$ | Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hg | A1Hg | µg/l | 0.12 | 0.14 | 0.14 | 0.14 | 0.02 | 15.5 | 25 | 12 | 83 |
| | G3Hg | µg/l | 0.039 | 0.043 | 0.045 | 0.042 | 0.007 | 15.9 | 30 | 13 | 55 |
| | N2Hg | µg/l | 0.075 | 0.076 | 0.076 | 0.075 | 0.011 | 14.3 | 25 | 13 | 82 |
| Mn | A1M | µg/l | 19.5 | 18.9 | 18.9 | 18.9 | 0.7 | 3.9 | 10 | 12 | 100 |
| | G3M | µg/l | 29.5 | 29.5 | 29.5 | 29.0 | 2.0 | 6.9 | 15 | 14 | 86 |
| | N2M | µg/l | 3.66 | 3.66 | 3.66 | 3.67 | 0.23 | 6.2 | 15 | 14 | 93 |
| Mo | A1M | µg/l | 21.5 | 20.8 | 20.8 | 21.0 | 1.0 | 4.9 | 10 | 10 | 100 |
| | G3M | µg/l | 16.5 | 16.5 | 16.5 | 16.0 | 1.2 | 7.0 | 15 | 10 | 90 |
| | N2M | µg/l | 10.2 | 10.3 | 10.3 | 10.2 | 0.7 | 6.6 | 15 | 11 | 91 |
| Ni | A1M | µg/l | 3.36 | 3.32 | 3.32 | 3.32 | 0.10 | 2.9 | 10 | 12 | 100 |
| | G3M | µg/l | 5.72 | 5.72 | 5.72 | 5.70 | 0.30 | 5.2 | 10 | 12 | 92 |
| | N2M | µg/l | 1.13 | 1.13 | 1.13 | 1.14 | 0.05 | 4.1 | 10 | 13 | 90 |
| Pb | A1M | µg/l | 7.21 | 6.97 | 7.01 | 7.01 | 0.26 | 3.7 | 10 | 11 | 91 |
| | G3M | µg/l | 2.79 | 2.64 | 2.67 | 2.67 | 0.14 | 5.1 | 15 | 11 | 82 |
| | N2M | µg/l | 5.26 | 5.01 | 5.05 | 5.07 | 0.23 | 4.5 | 15 | 12 | 83 |
| Sb | A1M | µg/l | 4.35 | 4.23 | 4.32 | 4.24 | 0.25 | 5.9 | 10 | 10 | 80 |
| | G3M | µg/l | 2.01 | 2.00 | 2.02 | 2.01 | 0.07 | 3.6 | 10 | 11 | 82 |
| | N2M | µg/l | 4.91 | 4.85 | 4.90 | 4.91 | 0.23 | 4.7 | 10 | 11 | 82 |
| Se | A1M | µg/l | 2.75 | 2.78 | 2.78 | 2.72 | 0.13 | 4.8 | 15 | 10 | 100 |
| | G3M | µg/l | 1.56 | 1.56 | 1.56 | 1.59 | 0.10 | 6.3 | 15 | 11 | 91 |
| | N2M | µg/l | 2.61 | 2.62 | 2.62 | 2.61 | 0.11 | 4.1 | 15 | 11 | 91 |
| Sr | A1M | µg/l | 35.5 | 34.7 | 35.2 | 33.9 | 2.0 | 5.6 | 10 | 8 | 88 |
| | G3M | µg/l | 100 | 100 | 100 | 100 | 2 | 2.1 | 10 | 9 | 89 |
| | N2M | µg/l | 43.3 | 43.3 | 43.8 | 42.9 | 2.0 | 4.6 | 10 | 9 | 78 |
| Ti | A1M | µg/l | 13.3 | 12.9 | 12.9 | 13.0 | 0.4 | 2.9 | 10 | 8 | 100 |
| | G3M | µg/l | 5.31 | 5.31 | - | 5.23 | - | - | 15 | 8 | 86 |
| | N2M | µg/l | 11.9 | 11.7 | 11.7 | 11.9 | 1.1 | 9.3 | 20 | 9 | 89 |
| U | A1M | µg/l | 6.30 | 5.93 | 5.93 | 5.88 | 0.32 | 5.3 | 10 | 10 | 90 |
| | G3M | µg/l | 1.85 | 1.85 | 1.83 | 1.75 | 0.15 | 8.1 | 20 | 11 | 73 |
| | N2M | µg/l | 4.37 | 4.37 | 4.43 | 4.26 | 0.33 | 7.5 | 15 | 11 | 82 |
| V | A1M | µg/l | 7.33 | 7.11 | 7.12 | 7.24 | 0.30 | 4.2 | 10 | 10 | 100 |
| | G3M | µg/l | 3.67 | 3.67 | 3.67 | 3.62 | 0.23 | 6.2 | 15 | 10 | 90 |
| | N2M | µg/l | 1.58 | 1.58 | 1.58 | 1.56 | 0.05 | 3.5 | 15 | 11 | 82 |
| Zn | A1M | µg/l | 23.3 | 23.5 | 23.5 | 23.7 | 1.2 | 5.0 | 10 | 11 | 100 |
| | G3M | µg/l | 28.5 | 28.7 | 28.5 | 28.5 | 3.2 | 11.3 | 20 | 12 | 75 |
| | N2M | µg/l | 3.18 | 3.20 | 3.27 | 3.18 | 0.33 | 10.0 | 15 | 12 | 73 |
| | | | | | | | | | | | |

Rob. mean: the robust mean, $s_{rob}$: the robust standard deviation, $s_{rob}$ %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, $n_{all}$: the number of the participants, Acc z %: the results (%), where $|z| \leq 2$.

## 3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurands in the PT. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 10. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5.

**Effect of measurement methods on elemental results**

Participants used mostly ICP-MS technique followed by ICP-OES technique for the measurements. Only one participant used FAAS technique for some measurands (Appendix 10). The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test. In the statistical treatment no significant differences were observed, when the number of results was high enough for the statistical comparison. Similarly, by visual comparison of the other results no clear difference was observed.

As a general note, a low recovery may be an indication of loss of measurand which can occur during sample pretreatment (e.g. volatilization during acid digestion). It may also be caused by incorrect background correction (ICP-OES) or matrix effects. Recoveries that are too high may be caused by spectral interferences (overlapping wavelengths in emission spectrometry, polyatomic or isobaric interferences in mass spectrometry), matrix effects or contamination. Matrix effects can often be overcome by matrix matching the calibration standards however this is often difficult with environmental samples since the elemental concentrations vary a lot even within the same sample type.

The most pragmatic approach to minimize matrix effects in ICP techniques is to ensure robust plasma conditions. Appropriate internal standardization should be used, especially with ICP-MS. Matching the ionization potential and mass of the internal standard with those of the analytes is always a compromise. The samples measured in this round had rather clean matrices, therefore not particularly challenging in this respect. ICP-OES typically does not require internal standardization for natural waters, if plasma conditions are robust enough.

The assessment of boron results was demanding in this round. Boron is poorly ionized in the ICP and is therefore one of the most insensitive elements. In addition, it displays poor wash-out characteristics resulting in a high carry-over. Therefore, it is important to monitor the blank signal at regular intervals during sample measurement. Internal standardization in ICP-MS is also difficult due to the low mass of both boron isotopes. The closest elements in mass, lithium and beryllium, are typically analytes of interest in environmental samples and therefore not suitable. However, enriched $^{6}Li$ is sometimes used as in internal standard. The neighbouring carbon peak $^{12}C$ may sometimes cause elevated background signals, as methanol or some other carbon containing substance is often added to the samples on-line to enhance the sensitivity of arsenic and selenium.

According to the results of this PT, most of the participant's results remained lower than the assigned values (calculated value) of As, Ba, Co, Mn, Mo, Pb (also G3M, N2M), Ti, U, and V for the sample A1M. However, the differences were generally within the reported measurement

uncertainties of the participants. Sample A1M was a synthetic sample with no matrix effects present. The participants should pay attention to the calibration procedures and the preparation of calibration solutions to minimize any systematic errors. Also, the use of internal standards should be carefully validated for all analytes.

**Effect of measurement methods on mercury results**

For the analysis of mercury, ICP-MS was the most often used method of analysis. That was followed by CV-AFS. Other used methods were CV-AAS, and CV-ICP-MS (Appendix 10). No differences between the used measuring methods were found based on visual estimation.

Like other metal determinations, mercury results are also affected by digestion procedures used (acids and oxidation reagents, their concentration, volumes and purities, digestion temperature and time). For natural water samples hydrochloric acid is recommended for sample preservation and BrCl is recommended for oxidation of mercury species.

Generally, the differences in mercury results are most likely due to different pretreatment procedures, provided a measurement technique sensitive enough is used. Cold vapour techniques are recommended, especially for natural water matrices with low concentrations. CV-AFS and CV-ICP-MS have superior detection capability compared to CV-AAS or CV-ICP-OES.

## 3.3 Uncertainties of the results

At maximum 88 % of the participants reported the expanded uncertainties ($k$=2) at least with some of their results (Table 2, Appendix 10). Several approaches were used for estimating the measurement uncertainty (Appendix 11). The most commonly used approach was based on the internal quality data with sample replicates and the method validation data [6]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at maximum five participants (Appendix 11) [6, 7]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The range of the reported uncertainties varied between the measurements and the sample types. As can be seen in Table 2, some of the participants have over-estimated their expanded ($k=2$) measurement uncertainty. Very high measurement uncertainties (i.e. 50 % or higher, bolded in Table 2) should not exist, unless the measured concentration is near to the limit of quantification. In this PT the participants did not report expanded uncertainties below 5 %, which could commonly be considered unrealistic uncertainty value for routine laboratories.

Table 2. The range of the expanded measurement uncertainties ($k$=2, $U_i$%) reported by the participants.

| Measurand | A1M/A1Hg, % | G3M/G3Hg, % | N2M/N2Hg, % |
|---|---|---|---|
| **Al** | 6-25 | 9-25 | 6-25 |
| **As** | 10-23 | 10-23 | 10-30 |
| **B** | 10-28 | 10-20 | 10-20 |
| **Ba** | 7-20 | 7-20 | 7-20 |
| **Cd** | 10-20 | 10-20 | 10-20 |
| **Co** | 10-20 | 10-20 | 10-20 |
| **Cr** | 10-22 | 10-22 | 10-27 |
| **Cu** | 6-20 | 6-20 | 6-20 |
| **Fe** | 7-35 | 7-35 | 7-35 |
| **Hg** | 15-25 | 8-25 | 8-25 |
| **Mn** | 7-20 | 8-27 | 8-20 |
| **Mo** | 10-26 | 10-26 | 10-26 |
| **Ni** | 10-**60** | 5-26 | 10-**60** |
| **Pb** | 10-38 | 10-25 | 10-38 |
| **Sb** | 10-20 | 10-25 | 10-20 |
| **Se** | 10-28 | 10-28 | 10-28 |
| **Sr** | 10-30 | 6-25 | 10-30 |
| **Ti** | 15-20 | 15-20 | 15-20 |
| **U** | 10-20 | 10-20 | 10-20 |
| **V** | 8-21 | 8-21 | 8-21 |
| **Zn** | 10-25 | 10-25 | 10-**50** |

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into the water quality registers have been published in Finland [8]. The recommendation for measurement uncertainties for majority of tested measurands in natural waters is 15 %, except for As 0.1 µg/l in sample N2M. For Mn, the recommended uncertainty is 3 µg/l at 10 µg/l concentration level [8]. In this proficiency test some of the participants had their measurement uncertainties within this limit, while some did not achieve it. However, harmonization of the uncertainties' estimation should be continued.

# 4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 7). The z scores were interpreted as follows:

| Criteria | Performance |
|---|---|
| $\lvert z \rvert \leq 2$ | Satisfactory |
| $2 < \lvert z \rvert < 3$ | Questionable |
| $\lvert z \rvert \geq 3$ | Unsatisfactory |

In total, 88 % of the results were satisfactory, when deviation 10–30 % from the assigned value was accepted.

Almost 88 % of the participants used accredited analytical methods at least for a part of the measurands and 89 % of their results were satisfactory. In the previous similar PTs for natural waters 90 % (MET 05/2018) and 89 % (MET 04/2019) of the results were satisfactory when deviation 10–25 % from the assigned value was accepted [5, 9]. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3.

The percentage of the satisfactory results varied between 83 % and 94 % for the tested sample types (Table 3). The share of the satisfactory results in the synthetic sample A1M was the lowest for B, about 78 %. In total the share was somewhat higher than in the previous proficiency tests in 2018 and 2019 (Table 3) [5, 9].

For As, Ba, Co, Cr, Cu, Mo, Ni, Se, and V ≥ 90 % of the results were satisfactory in the ground water sample G3M. For the natural (lake) water sample N2M ≥ 90 % of the results for Al, As, Ba, Cr, Cu, Fe, Mn, Mo, Ni, and Se were satisfactory. In this proficiency test the share of the satisfactory results was somewhat lower than in the previous similar proficiency tests (Table 3) [5, 9].

Table 3. Summary of the performance evaluation in the proficiency test MET 05/2020.

| Sample | Satisfactory results (%) | Accepted deviation from the assigned value (%) | Remarks |
|---|---|---|---|
| A1M, A1Hg | 94 | 10-25 | • Mainly good performance.<br>• Difficulties in measurements for B: < 80% satisfactory results.<br>• In the previous PTs MET 04/2019 and MET 05/2018 the performance was satisfactory for 89 % and 90 % of the results, when accepting deviation of 10-20 % from the assigned value, respectively [5, 9]. |
| G3M, G3Hg | 83 | 10-30 | • Difficulties in measurements for Hg, B, Fe, U and Zn: < 80% satisfactory results.<br>• In the previous PTs MET 04/2019 and MET 05/2018 the performance was satisfactory for 91 % and 86 % of the results, when accepting deviation of 15–25 and 10–25 % from the assigned value, respectively [5, 9]. |
| N2M, N2Hg | 85 | 10–25 | • Difficulties in measurements for B, Sr and Zn: < 80% satisfactory results.<br>• In the previous PT MET 05/2018 the performance was satisfactory for 90 % of the results [9]. |

# 5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of metals in natural waters in April-May 2020. The measurands for the synthetic sample and natural as well as ground water samples were: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V, and Zn. In total 16 participants joined in the PT.

The calculated values (NIST traceable) were used as the assigned values for the synthetic samples (A1M) except for B, Hg and Pb. For Hg and Pb in the samples AIM, A1Hg, N2M, N2Hg, G3M, and G3Hg the results based on metrologically traceable isotope dilution (ID) ICP-MS technique were used as assigned values. For the other samples and measurands the robust mean value, the mean or the median ($n_{stat} < 12$) of the participants' results was used as the assigned value.

The uncertainties of the calculated and the metrologically traceable assigned values for metals in the synthetic samples varied between 0.5 and 3 %. When using the robust mean, the mean or the median of the participant results as the assigned value, the uncertainties of the assigned values were between 1.4 and 7.2 %.

The evaluation of the performance was based on the z scores. In this PT, 88 % of the results were satisfactory, when deviation 10–30 % from the assigned value was accepted. About 88 % of the participants used accredited methods and 89 % of their results were satisfactory.

# 6 Summary in Finnish

Proftest SYKE järjesti ympäristönäytteitä analysoiville laboratorioille pätevyyskokeen huhti-toukokuussa 2020. Pätevyyskokeessa määritettiin synteettisistä näytteistä sekä talous- ja pohjavesinäytteistä testisuureet Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, U, V ja Zn. Pätevyyskokeessa oli yhteensä 16 osallistujaa.

Testisuureen vertailuarvona käytettiin joko laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Lyijylle ja elohopealle käytettiin vertailuarvona metrologisesti jäljitettävää pitoisuutta osalla testinäytteistä. Vertailuarvolle laskettiin laajennettu epävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli välillä 0,5–3 % laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 1,4–7,2 %.

Pätevyyden arviointi tehtiin z- arvojen avulla. Koko aineistossa hyväksyttäviä tuloksia z-arvoilla arvioituna oli 88 %, kun tulosten annettiin vaihdella 10–30 % vertailuarvosta. Noin 88 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 89 %.

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# APPENDIX 1: Participants in the proficiency test

| Country | Participant |
|---|---|
| **Finland** | Eurofins Ahma Oy, Oulu |
| | Eurofins Environment Testing Finland Oy, Lahti |
| | KVVY Tutkimus Oy, Tampere |
| | Kymen Ympäristölaboratorio Oy |
| | Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku |
| | Luonnonvarakeskus, Viikki B2-laboratorio |
| | MetropoliLab Oy |
| | Neste Corporation, Technology Center, Kilpilahti |
| | Savo-Karjalan Ympäristötutkimus Oy, Kuopio |
| | SeiLab Oy Seinäjoen toimipiste |
| | SGS Finland Oy, Kotka |
| | SYKE, Helsingin toimipaikka |
| | SYNLAB Analytics & Services Finland Oy |
| | Teollisuuden Voima Oyj |
| **Norway** | Eurofins Environment Norway A/S, Moss, Norway |
| **Sweden** | IVL, Svenska Miljöinstitutet AB, GÖTEBORG, Sweden |

# APPENDIX 2: Sample preparation

The synthetic samples A1M was prepared by diluting from the NIST traceable certified reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The water samples N2M and G3M were prepared by adding some separate metal solutions (Merck CertiPUR®) into the original water sample, if the original concentration was not high enough. Samples N2Hg and G3Hg were prepared by adding from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc., if the original concentration was not high enough.

| Measurand | | A1M µg/l | N2M µg/l | G3M µg/l | Measurand | | A1M µg/l | N2M µg/l | G3M µg/l |
|---|---|---|---|---|---|---|---|---|---|
| **Al** | Original | 1120 | 370 | 95 | **Mn** | Original | 195 | 3.7 | 30 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | - | - | | Addition | - | - | - |
| | Ass. value | 112 | 409 | 91.7 | | Ass. value | 19.5 | 3.66 | 29.5 |
| **As** | Original | 72.5 | 0.55 | 0.18 | **Mo** | Original | 215 | 0.35 | 1.4 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | - | 5 | | Addition | - | 10 | 15 |
| | Ass. value | 7.25 | 0.57 | 5.17 | | Ass. value | 21.5 | 10.2 | 16.5 |
| **B** | Original | 132.5 | 13 | 33 | **Ni** | Original | 33.5 | 1.4 | 1 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | - | - | | Addition | - | - | 5 |
| | Ass. value | 18.3 | 28.4 | 38.9 | | Ass. value | 3.36 | 1.13 | 5.72 |
| **Ba** | Original | 95 | 28 | 8.9 | **Pb** | Original | 72.5 | 0.26 | 0.77 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | - | - | | Addition | - | 5 | 2 |
| | Ass. value | 9.50 | 26.5 | 8.44 | | Ass. value | 7.21 | 5.26 | 2.79 |
| **Cd** | Original | 3.25 | 0.009 | 0.02 | **Sb** | Original | 43.5 | 0.1 | 0.03 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | 0.49 | 0.3 | | Addition | - | 5 | 2 |
| | Ass. value | 0.33 | 0.51 | 0.33 | | Ass. value | 4.35 | 4.91 | 2.01 |
| **Co** | Original | 13.5 | 0.08 | 0.13 | **Se** | Original | 27.5 | 0 | 0 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | 1 | 2 | | Addition | - | 2.5 | 1.5 |
| | Ass. value | 1.35 | 1.06 | 2.04 | | Ass. value | 2.75 | 2.61 | 1.56 |
| **Cr** | Original | 23.5 | 0.46 | 0.2 | **Sr** | Original | 355 | 47 | 110 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | 1 | 3 | | Addition | - | - | - |
| | Ass. value | 2.35 | 1.46 | 3.12 | | Ass. value | 35.5 | 43.3 | 100 |
| **Cu** | Original | 215 | 6.1 | 26 | **Ti** | Original | 133 | 13 | 0.3 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | - | - | | Addition | - | - | 5 |
| | Ass. value | 21.5 | 6.00 | 24.9 | | Ass. value | 13.3 | 11.9 | 5.31 |
| **Fe** | Original | 775 | 240 | 19 | **U** | Original | 63 | 0.21 | 1.9 |
| | Dilution | 10 | - | - | | Dilution | 10 | - | - |
| | Addition | - | - | 50 | | Addition | - | 4.29 | - |
| | Ass. value | 77.5 | 247 | 66.4 | | Ass. value | 6.30 | 4.37 | 1.85 |
| **V** | Original | 73.3 | 0.64 | 0.76 | | | | | |
| | Dilution | 10 | - | - | | | **A1Hg µg/l** | **N2Hg µg/l** | **G3Hg µg/l** |
| | Addition | - | 1 | 3 | | | | | |
| | Ass. value | 7.33 | 1.58 | 3.67 | | | | | |
| **Zn** | Original | 233 | 3.3 | 29 | **Hg** | Original | - | 0.001 | 0.002 |
| | Dilution | 10 | - | - | | Dilution | - | - | - |
| | Addition | - | - | - | | Addition | 0.125 | 0.075 | 0.038 |
| | Ass. value | 23.3 | 3.18 | 28.5 | | Ass. value | 0.12 | 0.075 | 0.039 |

Original = the original concentration, Dilution = the ratio of dilution, Addition = the addition concentration, Ass. value = the assigned value

# APPENDIX 3: Homogeneity of the samples

The homogeneity was checked for the selected samples and measurands as duplicate measurements.

**Criteria for homogeneity:**

**$s_{anal}/s_h<0.5$ and $s_{sam}^2<c$,** where

$s_h$ = standard deviation for the testing of homogeneity
$s_{anal}$ = analytical deviation, standard deviation of the results in a sub sample
$s_{sam}$ = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$,
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

| Measurand/Sample | Concentration [µg/l] [mg/kg] | n | $s_{pt}$ % | $s_h$% | $s_h$ | $s_{anal}$ | $s_{anal}/s_h$ | $s_{anal}/s_h<0.5$? | $s_{sam}^2$ | c | $s_{sam}^2<c$? |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cd/N2M | 0,54 | 3 | 7.5 | 2.6 | 0.041 | 0.007 | 0.167 | Yes | 0.000001 | 0.0006 | Yes |
| Cr/N2M | 1.46 | 3 | 7.5 | 2.1 | 0.110 | 0..015 | 0.134 | Yes | 0.0006 | 0.004 | Yes |
| Pb/N2M | 5.10 | 3 | 7.5 | 0.8 | 0.382 | 0.020 | 0.053 | Yes | 0.00001 | 0.041 | Yes |
| Se/N2M | 2.65 | 3 | 7.5 | 1.3 | 0.199 | 0.009 | 0.046 | Yes | 0.0006 | 0.011 | Yes |
| Zn/N2M | 3.16 | 3 | 7.5 | 3.0 | 0.237 | 0.046 | 0.194 | Yes | 0.0009 | 0.024 | Yes |
| Cd/G3M | 0.34 | 3 | 7.5 | 1.4 | 0.028 | 0.002 | 0.090 | Yes | 0 | 0.0002 | Yes |
| Cr/G3M | 3.12 | 3 | 7.5 | 1.7 | 0.234 | 0.026 | 0.111 | Yes | 0.0004 | 0.018 | Yes |
| Pb/G3M | 2.68 | 3 | 7.5 | 0.9 | 0.201 | 0.011 | 0.057 | Yes | 0.00001 | 0.011 | Yes |
| Se/G3M | 1.56 | 3 | 7.5 | 2.3 | 0.117 | 0.005 | 0.046 | Yes | 0.0004 | 0.004 | Yes |
| Zn/G3M | 29.4 | 3 | 10 | 7.1 | 2.935 | 0.336 | 0.115 | Yes | 1.638 | 2.807 | Yes |
| Hg/N2Hg* | 0.08 | 3 | 12.5 | 0.7 | 0.009 | 0.0003 | 0.027 | Yes | 0 | 0.00002 | Yes |
| Hg/G3Hg* | 0.04 | 3 | 15 | 1.0 | 0.006 | 0.0002 | 0.031 | Yes | 0 | 0.000009 | Yes |
| Pb/N2M* | 5.26 | 3 | 7.5 | 0.5 | 0.395 | 0.012 | 0.030 | Yes | 0 | 0.043 | Yes |
| Pb/G3M* | 2.79 | 3 | 7.5 | 0.8 | 0.209 | 0.010 | 0.047 | Yes | 0 | 0.012 | Yes |

*) result based on the ID-ICP-MS measurement

n = number of tested sub-samples
$s_{pt}$ % = standard deviation for proficiency assessment

**Conclusion:** The criteria were fulfilled for the tested measurands and the samples were regarded as homogenous.

# APPENDIX 4: Feedback from the proficiency test

## FEEDBACK FROM THE PARTICIPANTS

| Participant | Comments on technical excecution | Action / Proftest SYKE |
|---|---|---|
| 4 | The participant informed that the delivery of samples was delayed. | According to the distributor's (Posti) tracking system, the samples arrived to the participant on time. The provider recommends to check the internal package delivery procedures. |

| Participant | Comments to the results | Action / Proftest SYKE |
|---|---|---|
| 5 | The participant reported their results for sample N2M erroneously for the sample G3M and vice versa. | The reported results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the participant's results have been reported correctly, the results would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4]. |
| 6 | The participant reported their laboratory results via email. | The results should report only via the electronic client interface. The participant was advised to report the results via ProftestWEB and the results were received in correct form. |

# APPENDIX 5: Evaluation of the assigned values and their uncertainties

| Measurand | Sample | Unit | Assigned value | $U_{pt}$ | $U_{pt}$, % | Evaluation method of assigned value | $u_{pt}/s_{pt}$ |
|---|---|---|---|---|---|---|---|
| Al | A1M | µg/l | 112 | 1 | 0.6 | Calculated value | 0.06 |
| | G3M | µg/l | 91.7 | 2.8 | 3.1 | Mean | 0.21 |
| | N2M | µg/l | 409 | 16 | 4.0 | Robust mean | 0.27 |
| As | A1M | µg/l | 7.25 | 0.06 | 0.8 | Calculated value | 0.08 |
| | G3M | µg/l | 5.17 | 0.08 | 1.5 | Mean | 0.15 |
| | N2M | µg/l | 0.57 | 0.01 | 1.6 | Mean | 0.16 |
| B | A1M | µg/l | 18.3 | 1.4 | 7.9 | Median | 0.32 |
| | G3M | µg/l | 38.9 | 1.9 | 4.9 | Median | 0.20 |
| | N2M | µg/l | 28.4 | 1.7 | 6.1 | Median | 0.24 |
| Ba | A1M | µg/l | 9.50 | 0.07 | 0.7 | Calculated value | 0.07 |
| | G3M | µg/l | 8.44 | 0.17 | 2.0 | Mean | 0.13 |
| | N2M | µg/l | 26.5 | 0.5 | 2.0 | Mean | 0.20 |
| Cd | A1M | µg/l | 0.33 | <0.01 | 0.6 | Calculated value | 0.04 |
| | G3M | µg/l | 0.33 | 0.01 | 3.9 | Median | 0.26 |
| | N2M | µg/l | 0.51 | 0.01 | 2.0 | Median | 0.13 |
| Co | A1M | µg/l | 1.35 | 0.01 | 0.5 | Calculated value | 0.05 |
| | G3M | µg/l | 2.04 | 0.06 | 3.1 | Mean | 0.21 |
| | N2M | µg/l | 1.06 | 0.03 | 3.1 | Median | 0.21 |
| Cr | A1M | µg/l | 2.35 | 0.02 | 0.7 | Calculated value | 0.05 |
| | G3M | µg/l | 3.12 | 0.06 | 2.0 | Mean | 0.13 |
| | N2M | µg/l | 1.46 | 0.03 | 1.8 | Mean | 0.12 |
| Cu | A1M | µg/l | 21.5 | 0.1 | 0.6 | Calculated value | 0.06 |
| | G3M | µg/l | 24.9 | 0.8 | 3.4 | Robust mean | 0.23 |
| | N2M | µg/l | 6.00 | 0.08 | 1.4 | Median | 0.09 |
| Fe | A1M | µg/l | 77.5 | 0.6 | 0.8 | Calculated value | 0.08 |
| | G3M | µg/l | 66.4 | 2.7 | 4.1 | Robust mean | 0.27 |
| | N2M | µg/l | 247 | 6 | 2.4 | Robust mean | 0.24 |
| Hg | A1Hg | µg/l | 0.12 | <0.01 | 3.0 | ID-ICP-MS | 0.12 |
| | G3Hg | µg/l | 0.039 | 0.001 | 3.0 | ID-ICP-MS | 0.10 |
| | N2Hg | µg/l | 0.075 | 0.002 | 3.0 | ID-ICP-MS | 0.12 |
| Mn | A1M | µg/l | 19.5 | 0.1 | 0.7 | Calculated value | 0.07 |
| | G3M | µg/l | 29.5 | 1.5 | 5.0 | Robust mean | 0.33 |
| | N2M | µg/l | 3.66 | 0.16 | 4.3 | Robust mean | 0.29 |
| Mo | A1M | µg/l | 21.5 | 0.1 | 0.6 | Calculated value | 0.06 |
| | G3M | µg/l | 16.5 | 0.7 | 4.1 | Mean | 0.27 |
| | N2M | µg/l | 10.2 | 0.4 | 3.7 | Median | 0.25 |
| Ni | A1M | µg/l | 3.36 | 0.02 | 0.6 | Calculated value | 0.06 |
| | G3M | µg/l | 5.72 | 0.16 | 2.8 | Mean | 0.28 |
| | N2M | µg/l | 1.13 | 0.03 | 2.4 | Mean | 0.24 |
| Pb | A1M | µg/l | 7.21 | 0.18 | 2.5 | ID-ICP-MS | 0.25 |
| | G3M | µg/l | 2.79 | 0.07 | 2.5 | ID-ICP-MS | 0.17 |
| | N2M | µg/l | 5.26 | 0.13 | 2.5 | ID-ICP-MS | 0.17 |
| Sb | A1M | µg/l | 4.35 | 0.03 | 0.8 | Calculated value | 0.08 |
| | G3M | µg/l | 2.01 | 0.04 | 2.0 | Median | 0.20 |
| | N2M | µg/l | 4.91 | 0.13 | 2.6 | Median | 0.26 |

| Measurand | Sample | Unit | Assigned value | $U_{pt}$ | $U_{pt}$, % | Evaluation method of assigned value | $u_{pt}/s_{pt}$ |
|---|---|---|---|---|---|---|---|
| Se | A1M | µg/l | 2.75 | 0.02 | 0.8 | Calculated value | 0.05 |
| | G3M | µg/l | 1.56 | 0.05 | 3.5 | Mean | 0.23 |
| | N2M | µg/l | 2.61 | 0.06 | 2.3 | Median | 0.15 |
| Sr | A1M | µg/l | 35.5 | 0.2 | 0.6 | Calculated value | 0.06 |
| | G3M | µg/l | 100 | 2 | 1.9 | Mean | 0.19 |
| | N2M | µg/l | 43.3 | 1.0 | 2.4 | Mean | 0.24 |
| Ti | A1M | µg/l | 13.3 | 0.1 | 0.7 | Calculated value | 0.07 |
| | G3M | µg/l | 5.31 | 0.25 | 4.8 | Mean | 0.32 |
| | N2M | µg/l | 11.9 | 0.7 | 5.8 | Median | 0.29 |
| U | A1M | µg/l | 6.30 | 0.05 | 0.8 | Calculated value | 0.08 |
| | G3M | µg/l | 1.85 | 0.12 | 6.3 | Mean | 0.32 |
| | N2M | µg/l | 4.37 | 0.17 | 3.8 | Mean | 0.25 |
| V | A1M | µg/l | 7.33 | 0.05 | 0.7 | Calculated value | 0.07 |
| | G3M | µg/l | 3.67 | 0.13 | 3.6 | Mean | 0.24 |
| | N2M | µg/l | 1.58 | 0.04 | 2.5 | Mean | 0.17 |
| Zn | A1M | µg/l | 23.3 | 0.1 | 0.6 | Calculated value | 0.06 |
| | G3M | µg/l | 28.5 | 2.1 | 7.2 | Median | 0.36 |
| | N2M | µg/l | 3.18 | 0.17 | 5.2 | Median | 0.35 |

$U_{pt}$ = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
$s_{pt}$= the standard deviation for proficiency assessment
$u_{pt}$= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

# APPENDIX 6: Terms in the results tables

**Results of each participant**

| | |
|---|---|
| **Measurand** | The tested parameter |
| **Sample** | The code of the sample |
| **z score** | Calculated as follows:<br>$z = (x_i - x_{pt})/s_{pt}$, where<br>$x_i$ = the result of the individual participant<br>$x_{pt}$ = the assigned value<br>$s_{pt}$ = the standard deviation for proficiency assessment |
| **Assigned value** | The value attributed to a particular property of a proficiency test item |
| **2 × $s_{pt}$ %** | The standard deviation for proficiency assessment ($s_{pt}$) at the 95 % confidence level |
| **Participant's result** | The result reported by the participant (the mean value of the replicates) |
| **Md** | Median |
| **s** | Standard deviation |
| **s %** | Standard deviation, % |
| **$n_{stat}$** | Number of results in statistical processing |

**Summary on the z scores**

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ( $2< z < 3$), positive error, the result deviates more than 2 × $s_{pt}$ from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × $s_{pt}$ from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × $s_{pt}$ from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × $s_{pt}$ from the assigned value

**Robust analysis**

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for $x^*$ and $s^*$ are calculated as:
$x^*$ = median of $x_i$ ($i = 1, 2, \ldots, p$)
$s^*$ = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

The mean $x^*$ and $s^*$ are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result $x_i$ $(i = 1, 2 \ldots p)$:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of $x^*$ and $s^*$ are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates $x^*$ and $s^*$ can be derived by an iterative calculation, i.e. by updating the values of $x^*$ and $s^*$ several times, until the process convergences [2].

# APPENDIX 7: Results of each participant

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | -0.36 | 112 | 10 | 110 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | 0.48 | 91.7 | 15 | 95.0 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | -0.29 | 409 | 15 | 400 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -1.52 | 7.25 | 10 | 6.70 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | 0.12 | 5.17 | 10 | 5.20 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 0.35 | 0.57 | 10 | 0.58 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| Ba | µg/l | A1M | | -0.63 | 9.50 | 10 | 9.20 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | 0.57 | 8.44 | 15 | 8.80 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | 1.13 | 26.5 | 10 | 28.0 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | -0.40 | 0.33 | 15 | 0.32 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | 0.00 | 0.33 | 15 | 0.33 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | 0.26 | 0.51 | 15 | 0.52 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -0.74 | 1.35 | 10 | 1.30 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | 1.05 | 2.04 | 15 | 2.20 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | 0.50 | 1.06 | 15 | 1.10 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | -0.28 | 2.35 | 15 | 2.30 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | 0.77 | 3.12 | 15 | 3.30 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | 0.37 | 1.46 | 15 | 1.50 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -0.47 | 21.5 | 10 | 21.0 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | 0.59 | 24.9 | 15 | 26.0 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | 0.00 | 6.00 | 15 | 6.00 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -0.90 | 77.5 | 10 | 74.0 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 0.32 | 66.4 | 15 | 68.0 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | -0.57 | 247 | 10 | 240 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 2.00 | 0.12 | 25 | 0.15 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | | 0.039 | 30 | *<0.10* | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | | 0.075 | 25 | *<0.10* | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | 0.51 | 19.5 | 10 | 20.0 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | 1.13 | 29.5 | 15 | 32.0 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 0.87 | 3.66 | 15 | 3.90 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | -0.47 | 21.5 | 10 | 21.0 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | 0.40 | 16.5 | 15 | 17.0 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | 1.05 | 10.2 | 15 | 11.0 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | -0.36 | 3.36 | 10 | 3.30 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | 0.98 | 5.72 | 10 | 6.00 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | -0.53 | 1.13 | 10 | 1.10 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -1.41 | 7.21 | 10 | 6.70 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -0.43 | 2.79 | 15 | 2.70 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -0.66 | 5.26 | 15 | 5.00 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | 0.23 | 4.35 | 10 | 4.40 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 0.90 | 2.01 | 10 | 2.10 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | 0.77 | 4.91 | 10 | 5.10 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | -0.24 | 2.75 | 15 | 2.70 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | 1.20 | 1.56 | 15 | 1.70 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | -0.05 | 2.61 | 15 | 2.60 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Ti | µg/l | A1M | | -0.45 | 13.3 | 10 | 13.0 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | 0.23 | 5.31 | 15 | 5.40 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | -0.76 | 11.9 | 20 | 11.0 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | -0.95 | 6.30 | 10 | 6.00 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | 0.27 | 1.85 | 20 | 1.90 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | 1.01 | 4.37 | 15 | 4.70 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | 0.19 | 7.33 | 10 | 7.40 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | 1.20 | 3.67 | 15 | 4.00 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | 1.01 | 1.58 | 15 | 1.70 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | -0.26 | 23.3 | 10 | 23.0 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | 0.18 | 28.5 | 20 | 29.0 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | 0.08 | 3.18 | 15 | 3.20 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 2 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | 0.06 | 112 | 10 | 112 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | -0.47 | 91.7 | 15 | 88.5 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.16 | 409 | 15 | 414 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.27 | 7.25 | 10 | 7.15 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | 0.73 | 5.17 | 10 | 5.36 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 1.02 | 0.57 | 10 | 0.60 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | -7.20 | 18.3 | 25 | 1.8 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | -3.27 | 38.9 | 25 | 23.0 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | -4.70 | 28.4 | 25 | 11.7 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -1.11 | 9.50 | 10 | 8.97 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | -0.39 | 8.44 | 15 | 8.19 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -0.10 | 26.5 | 10 | 26.4 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | 0.24 | 0.33 | 15 | 0.34 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | 0.24 | 0.33 | 15 | 0.34 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | 0.42 | 0.51 | 15 | 0.53 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -1.23 | 1.35 | 10 | 1.27 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | -0.56 | 2.04 | 15 | 1.96 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | -0.79 | 1.06 | 15 | 1.00 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | -0.22 | 2.35 | 15 | 2.31 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | -0.06 | 3.12 | 15 | 3.11 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | -0.09 | 1.46 | 15 | 1.45 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -0.49 | 21.5 | 10 | 21.0 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | -0.15 | 24.9 | 15 | 24.6 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | -0.42 | 6.00 | 15 | 5.81 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -1.38 | 77.5 | 10 | 72.2 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | -0.99 | 66.4 | 15 | 61.5 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.11 | 247 | 10 | 248 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 0.87 | 0.12 | 25 | 0.13 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 1.37 | 0.039 | 30 | 0.047 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | 0.32 | 0.075 | 25 | 0.078 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -1.18 | 19.5 | 10 | 18.3 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -0.73 | 29.5 | 15 | 27.9 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | -0.55 | 3.66 | 15 | 3.51 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |

| Participant 2 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Mo | µg/l | A1M | | -1.95 | 21.5 | 10 | 19.4 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | -0.49 | 16.5 | 15 | 15.9 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | -0.55 | 10.2 | 15 | 9.8 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | 0.23 | 3.36 | 10 | 3.40 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | 0.71 | 5.72 | 10 | 5.92 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | 0.92 | 1.13 | 10 | 1.18 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -1.41 | 7.21 | 10 | 6.70 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -1.48 | 2.79 | 15 | 2.48 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -1.47 | 5.26 | 15 | 4.68 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | -0.80 | 4.35 | 10 | 4.18 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 0.31 | 2.01 | 10 | 2.04 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | 0.13 | 4.91 | 10 | 4.94 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | 0.89 | 2.75 | 15 | 2.93 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | 0.29 | 1.56 | 15 | 1.59 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | 0.90 | 2.61 | 15 | 2.79 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | A1M | | -0.94 | 35.5 | 10 | 33.8 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | -0.31 | 100 | 10 | 98 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | -0.19 | 43.3 | 10 | 42.9 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | A1M | | 0.12 | 13.3 | 10 | 13.4 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | -0.13 | 5.31 | 15 | 5.26 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | 0.37 | 11.9 | 20 | 12.3 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | -1.85 | 6.30 | 10 | 5.72 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | -0.63 | 1.85 | 20 | 1.73 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -0.51 | 4.37 | 15 | 4.20 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -1.23 | 7.33 | 10 | 6.88 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | -0.62 | 3.67 | 15 | 3.50 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | -0.15 | 1.58 | 15 | 1.56 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | 1.53 | 23.3 | 10 | 25.1 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | 0.14 | 28.5 | 20 | 28.9 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | 1.98 | 3.18 | 15 | 3.65 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 3 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | 0.18 | 112 | 10 | 113 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | -0.09 | 91.7 | 15 | 91.1 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.39 | 409 | 15 | 421 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.52 | 7.25 | 10 | 7.06 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | -0.39 | 5.17 | 10 | 5.07 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 0.56 | 0.57 | 10 | 0.59 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | 0.00 | 18.3 | 25 | 18.3 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | -0.33 | 38.9 | 25 | 37.3 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | -0.31 | 28.4 | 25 | 27.3 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -0.80 | 9.50 | 10 | 9.12 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | -0.33 | 8.44 | 15 | 8.23 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -0.60 | 26.5 | 10 | 25.7 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | -0.48 | 0.33 | 15 | 0.32 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | -1.29 | 0.33 | 15 | 0.30 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | -0.78 | 0.51 | 15 | 0.48 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |

| Participant 3 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Co | µg/l | A1M | | -0.30 | 1.35 | 10 | 1.33 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | -0.33 | 2.04 | 15 | 1.99 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | 0.00 | 1.06 | 15 | 1.06 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | 0.45 | 2.35 | 15 | 2.43 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | 0.51 | 3.12 | 15 | 3.24 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | 0.73 | 1.46 | 15 | 1.54 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -0.74 | 21.5 | 10 | 20.7 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | -0.11 | 24.9 | 15 | 24.7 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | -0.38 | 6.00 | 15 | 5.83 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -0.15 | 77.5 | 10 | 76.9 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 0.38 | 66.4 | 15 | 68.3 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.32 | 247 | 10 | 251 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 1.00 | 0.12 | 25 | 0.14 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 0.22 | 0.039 | 30 | 0.040 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | 0.58 | 0.075 | 25 | 0.080 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -0.92 | 19.5 | 10 | 18.6 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -0.27 | 29.5 | 15 | 28.9 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 0.04 | 3.66 | 15 | 3.67 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | -1.40 | 21.5 | 10 | 20.0 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | -1.29 | 16.5 | 15 | 14.9 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | -0.13 | 10.2 | 15 | 10.1 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | -0.77 | 3.36 | 10 | 3.23 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -0.73 | 5.72 | 10 | 5.51 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | -0.53 | 1.13 | 10 | 1.10 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -0.67 | 7.21 | 10 | 6.97 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -0.62 | 2.79 | 15 | 2.66 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -0.43 | 5.26 | 15 | 5.09 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | -0.87 | 4.35 | 10 | 4.16 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 0.00 | 2.01 | 10 | 2.01 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | -0.16 | 4.91 | 10 | 4.87 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | -0.39 | 2.75 | 15 | 2.67 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | -0.94 | 1.56 | 15 | 1.45 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | -0.72 | 2.61 | 15 | 2.47 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| U | µg/l | A1M | | -1.52 | 6.30 | 10 | 5.82 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | -0.54 | 1.85 | 20 | 1.75 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -0.34 | 4.37 | 15 | 4.26 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -0.19 | 7.33 | 10 | 7.26 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | 0.07 | 3.67 | 15 | 3.69 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | 0.25 | 1.58 | 15 | 1.61 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | -1.20 | 23.3 | 10 | 21.9 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | -1.37 | 28.5 | 20 | 24.6 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | -0.63 | 3.18 | 15 | 3.03 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 4 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | -1.96 | 112 | 10 | 101 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | -0.99 | 91.7 | 15 | 84.9 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | -1.04 | 409 | 15 | 377 | 415 | 409 | 21 | 5.1 | 13 |
| B | µg/l | A1M | | 0.87 | 18.3 | 25 | 20.3 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | 0.70 | 38.9 | 25 | 42.3 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | 0.68 | 28.4 | 25 | 30.8 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | 0.34 | 9.50 | 10 | 9.66 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | 0.27 | 8.44 | 15 | 8.61 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | 0.75 | 26.5 | 10 | 27.5 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cu | µg/l | A1M | | 0.65 | 21.5 | 10 | 22.2 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | 0.27 | 24.9 | 15 | 25.4 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | 0.40 | 6.00 | 15 | 6.18 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | 0.98 | 77.5 | 10 | 81.3 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 0.58 | 66.4 | 15 | 69.3 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.89 | 247 | 10 | 258 | 248 | 247 | 8 | 3.2 | 14 |
| Mn | µg/l | A1M | | -0.31 | 19.5 | 10 | 19.2 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | 0.05 | 29.5 | 15 | 29.6 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 0.15 | 3.66 | 15 | 3.70 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Ni | µg/l | A1M | | -0.12 | 3.36 | 10 | 3.34 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -1.05 | 5.72 | 10 | 5.42 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | | 1.13 | 10 | <2 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Sr | µg/l | A1M | | 3.10 | 35.5 | 10 | 41.0 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | 0.00 | 100 | 10 | 100 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | 2.63 | 43.3 | 10 | 49.0 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Zn | µg/l | A1M | | 0.86 | 23.3 | 10 | 24.3 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | 1.47 | 28.5 | 20 | 32.7 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | 0.92 | 3.18 | 15 | 3.40 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | 1.25 | 112 | 10 | 119 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | 45.12 | 91.7 | 15 | 402.0 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | -10.26 | 409 | 15 | 94 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.36 | 7.25 | 10 | 7.12 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | -17.85 | 5.17 | 10 | 0.56 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 162.46 | 0.57 | 10 | 5.20 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | -0.17 | 18.3 | 25 | 17.9 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | -2.28 | 38.9 | 25 | 27.8 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | 2.90 | 28.4 | 25 | 38.7 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | 0.29 | 9.50 | 10 | 9.64 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | 30.11 | 8.44 | 15 | 27.50 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -13.42 | 26.5 | 10 | 8.7 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | 0.16 | 0.33 | 15 | 0.33 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | 7.76 | 0.33 | 15 | 0.52 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | -4.63 | 0.51 | 15 | 0.33 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | 0.89 | 1.35 | 10 | 1.41 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | -6.14 | 2.04 | 15 | 1.10 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | 13.71 | 1.06 | 15 | 2.15 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Cr | µg/l | A1M | | 0.17 | 2.35 | 15 | 2.38 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | -6.97 | 3.12 | 15 | 1.49 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | 17.81 | 1.46 | 15 | 3.41 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | 1.12 | 21.5 | 10 | 22.7 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | -9.87 | 24.9 | 15 | 6.5 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | 50.22 | 6.00 | 15 | 28.60 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | 0.44 | 77.5 | 10 | 79.2 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 36.67 | 66.4 | 15 | 249.0 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | -14.40 | 247 | 10 | 69 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 0.00 | 0.12 | 25 | 0.12 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 5.04 | 0.039 | 30 | 0.069 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | -3.45 | 0.075 | 25 | 0.043 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | 0.10 | 19.5 | 10 | 19.6 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -11.68 | 29.5 | 15 | 3.7 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 94.50 | 3.66 | 15 | 29.60 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | 0.00 | 21.5 | 10 | 21.5 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | -5.17 | 16.5 | 15 | 10.1 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | 7.71 | 10.2 | 15 | 16.1 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | 0.89 | 3.36 | 10 | 3.51 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -15.91 | 5.72 | 10 | 1.17 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | 85.31 | 1.13 | 10 | 5.95 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -0.22 | 7.21 | 10 | 7.13 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | 11.28 | 2.79 | 15 | 5.15 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -6.44 | 5.26 | 15 | 2.72 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | -0.51 | 4.35 | 10 | 4.24 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 27.96 | 2.01 | 10 | 4.82 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | -11.89 | 4.91 | 10 | 1.99 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | 0.73 | 2.75 | 15 | 2.90 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | 10.09 | 1.56 | 15 | 2.74 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | -4.80 | 2.61 | 15 | 1.67 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | A1M | | 0.28 | 35.5 | 10 | 36.0 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | -11.16 | 100 | 10 | 44 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | 26.65 | 43.3 | 10 | 101.0 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | A1M | | -0.45 | 13.3 | 10 | 13.0 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | 17.05 | 5.31 | 15 | 12.10 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | -5.98 | 11.9 | 20 | 4.8 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | -0.44 | 6.30 | 10 | 6.16 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | 14.54 | 1.85 | 20 | 4.54 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -7.66 | 4.37 | 15 | 1.86 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | 0.22 | 7.33 | 10 | 7.41 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | -7.45 | 3.67 | 15 | 1.62 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | 17.97 | 1.58 | 15 | 3.71 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | 1.03 | 23.3 | 10 | 24.5 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | -8.81 | 28.5 | 20 | 3.4 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | 109.52 | 3.18 | 15 | 29.30 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 6 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Hg | µg/l | A1Hg | | 1.87 | 0.12 | 25 | 0.15 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 5.68 | 0.039 | 30 | 0.072 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | 1.40 | 0.075 | 25 | 0.088 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |

| Participant 7 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | 1.07 | 112 | 10 | 118 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | 0.65 | 91.7 | 15 | 96.2 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | -0.68 | 409 | 15 | 388 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.74 | 7.25 | 10 | 6.98 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | 0.27 | 5.17 | 10 | 5.24 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 0.07 | 0.57 | 10 | 0.57 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | -0.17 | 18.3 | 25 | 17.9 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | -0.27 | 38.9 | 25 | 37.6 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | -0.23 | 28.4 | 25 | 27.6 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -1.41 | 9.50 | 10 | 8.83 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | -0.02 | 8.44 | 15 | 8.43 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -0.45 | 26.5 | 10 | 25.9 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | -0.08 | 0.33 | 15 | 0.33 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | -0.04 | 0.33 | 15 | 0.33 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | 0.37 | 0.51 | 15 | 0.52 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | 0.44 | 1.35 | 10 | 1.38 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | -0.13 | 2.04 | 15 | 2.02 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | 0.13 | 1.06 | 15 | 1.07 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | 0.06 | 2.35 | 15 | 2.36 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | -0.34 | 3.12 | 15 | 3.04 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | -0.18 | 1.46 | 15 | 1.44 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | 0.65 | 21.5 | 10 | 22.2 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | -0.32 | 24.9 | 15 | 24.3 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | 0.04 | 6.00 | 15 | 6.02 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -0.08 | 77.5 | 10 | 77.2 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 0.16 | 66.4 | 15 | 67.2 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | -0.49 | 247 | 10 | 241 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 0.20 | 0.12 | 25 | 0.12 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 0.09 | 0.039 | 30 | 0.040 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | -0.18 | 0.075 | 25 | 0.073 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -0.72 | 19.5 | 10 | 18.8 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -0.32 | 29.5 | 15 | 28.8 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | -0.29 | 3.66 | 15 | 3.58 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | -0.37 | 21.5 | 10 | 21.1 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | 0.65 | 16.5 | 15 | 17.3 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | 0.52 | 10.2 | 15 | 10.6 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | 0.24 | 3.36 | 10 | 3.40 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -0.63 | 5.72 | 10 | 5.54 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | 0.18 | 1.13 | 10 | 1.14 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | 0.31 | 7.21 | 10 | 7.32 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -0.05 | 2.79 | 15 | 2.78 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -0.15 | 5.26 | 15 | 5.20 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |

| Participant 7 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Sb | µg/l | A1M | | -0.51 | 4.35 | 10 | 4.24 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 0.20 | 2.01 | 10 | 2.03 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | 0.00 | 4.91 | 10 | 4.91 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | -0.15 | 2.75 | 15 | 2.72 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | -0.17 | 1.56 | 15 | 1.54 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | 0.05 | 2.61 | 15 | 2.62 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | A1M | | -1.13 | 35.5 | 10 | 33.5 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | -0.26 | 100 | 10 | 99 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | -0.42 | 43.3 | 10 | 42.4 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | A1M | | -0.60 | 13.3 | 10 | 12.9 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | -0.45 | 5.31 | 15 | 5.13 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | -1.43 | 11.9 | 20 | 10.2 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | 0.32 | 6.30 | 10 | 6.40 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | 0.65 | 1.85 | 20 | 1.97 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | 1.16 | 4.37 | 15 | 4.75 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -0.11 | 7.33 | 10 | 7.29 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | -0.18 | 3.67 | 15 | 3.62 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | 0.08 | 1.58 | 15 | 1.59 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | 0.34 | 23.3 | 10 | 23.7 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | -0.70 | 28.5 | 20 | 26.5 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | -0.08 | 3.18 | 15 | 3.16 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | G3M | | 1.21 | 91.7 | 15 | 100.0 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.68 | 409 | 15 | 430 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | G3M | | -0.66 | 5.17 | 10 | 5.00 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | -0.70 | 0.57 | 10 | 0.55 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | G3M | | -0.60 | 38.9 | 25 | 36.0 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | -7.24 | 28.4 | 25 | 2.7 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | G3M | | -0.22 | 8.44 | 15 | 8.30 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -0.38 | 26.5 | 10 | 26.0 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | G3M | | -1.21 | 0.33 | 15 | 0.30 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | -0.26 | 0.51 | 15 | 0.50 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | G3M | | -0.26 | 2.04 | 15 | 2.00 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | -0.75 | 1.06 | 15 | 1.00 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | G3M | | -0.51 | 3.12 | 15 | 3.00 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | 0.37 | 1.46 | 15 | 1.50 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | G3M | | 0.05 | 24.9 | 15 | 25.0 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | -0.44 | 6.00 | 15 | 5.80 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | G3M | | -11.97 | 66.4 | 15 | 6.8 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.24 | 247 | 10 | 250 | 248 | 247 | 8 | 3.2 | 14 |
| Mn | µg/l | G3M | | -11.93 | 29.5 | 15 | 3.1 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 0.51 | 3.66 | 15 | 3.80 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | G3M | | -0.40 | 16.5 | 15 | 16.0 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | -1.18 | 10.2 | 15 | 9.3 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | G3M | | 0.98 | 5.72 | 10 | 6.00 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | -0.53 | 1.13 | 10 | 1.10 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Pb | µg/l | G3M | | -0.91 | 2.79 | 15 | 2.60 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -1.17 | 5.26 | 15 | 4.80 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | G3M | | -0.10 | 2.01 | 10 | 2.00 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | 0.37 | 4.91 | 10 | 5.00 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | G3M | | 0.34 | 1.56 | 15 | 1.60 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | 0.46 | 2.61 | 15 | 2.70 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | G3M | | 0.00 | 100 | 10 | 100 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | -0.14 | 43.3 | 10 | 43.0 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | G3M | | -0.78 | 5.31 | 15 | 5.00 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | 0.08 | 11.9 | 20 | 12.0 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | G3M | | -2.43 | 1.85 | 20 | 1.40 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -0.52 | 4.37 | 15 | 4.20 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | G3M | | 1.20 | 3.67 | 15 | 4.00 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | -11.65 | 1.58 | 15 | 0.20 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | G3M | | -4.39 | 28.5 | 20 | 16.0 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | -13.33 | 3.18 | 15 | 0.00 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 9 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | -3.59 | 112 | 10 | 92 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | -2.92 | 91.7 | 15 | 71.6 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | -0.95 | 409 | 15 | 380 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.97 | 7.25 | 10 | 6.90 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | 0.12 | 5.17 | 10 | 5.20 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 0.00 | 0.57 | 10 | 0.57 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | -4.24 | 18.3 | 25 | 8.6 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | -3.17 | 38.9 | 25 | 23.5 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | -3.72 | 28.4 | 25 | 15.2 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Cd | µg/l | A1M | | 3.64 | 0.33 | 15 | 0.42 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | 3.64 | 0.33 | 15 | 0.42 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | 4.44 | 0.51 | 15 | 0.68 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Cr | µg/l | A1M | | -0.40 | 2.35 | 15 | 2.28 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | -0.51 | 3.12 | 15 | 3.00 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | -0.46 | 1.46 | 15 | 1.41 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -3.16 | 21.5 | 10 | 18.1 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | -1.23 | 24.9 | 15 | 22.6 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | -1.71 | 6.00 | 15 | 5.23 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -3.54 | 77.5 | 10 | 63.8 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | -2.59 | 66.4 | 15 | 53.5 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | -1.05 | 247 | 10 | 234 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 2.00 | 0.12 | 25 | 0.15 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 1.88 | 0.039 | 30 | 0.050 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | 1.60 | 0.075 | 25 | 0.090 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -1.85 | 19.5 | 10 | 17.7 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -1.04 | 29.5 | 15 | 27.2 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | -1.53 | 3.66 | 15 | 3.24 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |

| Participant 9 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Ni | µg/l | A1M | | -1.13 | 3.36 | 10 | 3.17 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -1.22 | 5.72 | 10 | 5.37 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | -1.06 | 1.13 | 10 | 1.07 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | 4.41 | 7.21 | 10 | 8.80 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | 2.34 | 2.79 | 15 | 3.28 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | 2.48 | 5.26 | 15 | 6.24 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | 5.43 | 4.35 | 10 | 5.53 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 6.77 | 2.01 | 10 | 2.69 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | 6.97 | 4.91 | 10 | 6.62 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | 1.02 | 2.75 | 15 | 2.96 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | 0.17 | 1.56 | 15 | 1.58 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | 0.36 | 2.61 | 15 | 2.68 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| U | µg/l | A1M | | -1.87 | 6.30 | 10 | 5.71 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | 2.05 | 1.85 | 20 | 2.23 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | 3.60 | 4.37 | 15 | 5.55 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |

| Participant 10 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | 0.36 | 112 | 10 | 114 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | 0.22 | 91.7 | 15 | 93.2 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | -0.75 | 409 | 15 | 386 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -1.68 | 7.25 | 10 | 6.64 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | -0.50 | 5.17 | 10 | 5.04 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | -0.49 | 0.57 | 10 | 0.56 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| Ba | µg/l | A1M | | -0.13 | 9.50 | 10 | 9.44 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | 0.13 | 8.44 | 15 | 8.52 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | 0.08 | 26.5 | 10 | 26.6 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | 0.40 | 0.33 | 15 | 0.34 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | 0.61 | 0.33 | 15 | 0.35 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | 0.31 | 0.51 | 15 | 0.52 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -0.44 | 1.35 | 10 | 1.32 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | 0.13 | 2.04 | 15 | 2.06 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | 0.63 | 1.06 | 15 | 1.11 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | 1.13 | 2.35 | 15 | 2.55 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | 0.17 | 3.12 | 15 | 3.16 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | -0.37 | 1.46 | 15 | 1.42 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -0.28 | 21.5 | 10 | 21.2 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | 0.43 | 24.9 | 15 | 25.7 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | 0.29 | 6.00 | 15 | 6.13 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | 1.16 | 77.5 | 10 | 82.0 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 0.02 | 66.4 | 15 | 66.5 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | -0.49 | 247 | 10 | 241 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 1.53 | 0.12 | 25 | 0.14 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 0.68 | 0.039 | 30 | 0.043 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | -0.21 | 0.075 | 25 | 0.073 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -0.51 | 19.5 | 10 | 19.0 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -0.18 | 29.5 | 15 | 29.1 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 0.07 | 3.66 | 15 | 3.68 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |

| Participant 10 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Mo | µg/l | A1M | | -0.74 | 21.5 | 10 | 20.7 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | -0.48 | 16.5 | 15 | 15.9 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | 0.00 | 10.2 | 15 | 10.2 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | -0.18 | 3.36 | 10 | 3.33 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | 0.21 | 5.72 | 10 | 5.78 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | 0.88 | 1.13 | 10 | 1.18 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -0.53 | 7.21 | 10 | 7.02 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -0.38 | 2.79 | 15 | 2.71 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -0.25 | 5.26 | 15 | 5.16 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | 5.01 | 4.35 | 10 | 5.44 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | -0.40 | 2.01 | 10 | 1.97 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | -1.10 | 4.91 | 10 | 4.64 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | -0.29 | 2.75 | 15 | 2.69 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | -0.77 | 1.56 | 15 | 1.47 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | -0.26 | 2.61 | 15 | 2.56 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | A1M | | -0.90 | 35.5 | 10 | 33.9 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | -0.66 | 100 | 10 | 97 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | -0.51 | 43.3 | 10 | 42.2 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | A1M | | -0.45 | 13.3 | 10 | 13.0 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | -0.28 | 5.31 | 15 | 5.20 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | -0.84 | 11.9 | 20 | 10.9 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | -2.29 | 6.30 | 10 | 5.58 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | -0.59 | 1.85 | 20 | 1.74 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -0.92 | 4.37 | 15 | 4.07 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -0.25 | 7.33 | 10 | 7.24 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | -0.51 | 3.67 | 15 | 3.53 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | -0.34 | 1.58 | 15 | 1.54 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | -0.60 | 23.3 | 10 | 22.6 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | -0.39 | 28.5 | 20 | 27.4 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | -0.42 | 3.18 | 15 | 3.08 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 11 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Cu | µg/l | G3M | | -1.12 | 24.9 | 15 | 22.8 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| Fe | µg/l | G3M | | 2.93 | 66.4 | 15 | 81.0 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.08 | 247 | 10 | 248 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 4.00 | 0.12 | 25 | 0.18 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 10.43 | 0.039 | 30 | 0.100 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | 5.87 | 0.075 | 25 | 0.130 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | G3M | | 1.18 | 29.5 | 15 | 32.1 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| Zn | µg/l | G3M | | 2.42 | 28.5 | 20 | 35.4 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |

| Participant 12 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | -0.18 | 112 | 10 | 111 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | -0.31 | 91.7 | 15 | 89.6 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.33 | 409 | 15 | 419 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.03 | 7.25 | 10 | 7.24 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | 0.15 | 5.17 | 10 | 5.21 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | -0.07 | 0.57 | 10 | 0.57 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | 0.74 | 18.3 | 25 | 20.0 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | 0.25 | 38.9 | 25 | 40.1 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | 0.34 | 28.4 | 25 | 29.6 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -0.84 | 9.50 | 10 | 9.10 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | -0.21 | 8.44 | 15 | 8.31 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -0.45 | 26.5 | 10 | 25.9 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | -0.85 | 0.33 | 15 | 0.31 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | -1.13 | 0.33 | 15 | 0.30 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | -0.29 | 0.51 | 15 | 0.50 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -1.48 | 1.35 | 10 | 1.25 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | -0.39 | 2.04 | 15 | 1.98 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | -0.38 | 1.06 | 15 | 1.03 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | -0.62 | 2.35 | 15 | 2.24 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | -0.09 | 3.12 | 15 | 3.10 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | -0.46 | 1.46 | 15 | 1.41 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -0.28 | 21.5 | 10 | 21.2 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | 0.11 | 24.9 | 15 | 25.1 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | -0.22 | 6.00 | 15 | 5.90 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -1.50 | 77.5 | 10 | 71.7 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | -0.44 | 66.4 | 15 | 64.2 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | -0.65 | 247 | 10 | 239 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | 6.07 | 0.12 | 25 | 0.21 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | 15.04 | 0.039 | 30 | 0.127 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | -1.19 | 0.075 | 25 | 0.064 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -1.44 | 19.5 | 10 | 18.1 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -1.13 | 29.5 | 15 | 27.0 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | -0.84 | 3.66 | 15 | 3.43 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | 0.65 | 21.5 | 10 | 22.2 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | 1.05 | 16.5 | 15 | 17.8 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | 1.18 | 10.2 | 15 | 11.1 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | -0.65 | 3.36 | 10 | 3.25 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -0.66 | 5.72 | 10 | 5.53 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | 0.18 | 1.13 | 10 | 1.14 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -1.25 | 7.21 | 10 | 6.76 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -1.43 | 2.79 | 15 | 2.49 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -1.04 | 5.26 | 15 | 4.85 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | -0.18 | 4.35 | 10 | 4.31 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | -1.19 | 2.01 | 10 | 1.89 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | -1.75 | 4.91 | 10 | 4.48 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | -0.34 | 2.75 | 15 | 2.68 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | -1.03 | 1.56 | 15 | 1.44 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | -0.56 | 2.61 | 15 | 2.50 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |

| Participant 12 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Sr | µg/l | A1M | | -1.01 | 35.5 | 10 | 33.7 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | 0.00 | 100 | 10 | 100 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | -0.46 | 43.3 | 10 | 42.3 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | A1M | | -1.20 | 13.3 | 10 | 12.5 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | 1.46 | 5.31 | 15 | 5.89 | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | -0.08 | 11.9 | 20 | 11.8 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | -1.17 | 6.30 | 10 | 5.93 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | -0.81 | 1.85 | 20 | 1.70 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -0.09 | 4.37 | 15 | 4.34 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -0.85 | 7.33 | 10 | 7.02 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | -0.62 | 3.67 | 15 | 3.50 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | -0.25 | 1.58 | 15 | 1.55 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | -1.12 | 23.3 | 10 | 22.0 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | -1.12 | 28.5 | 20 | 25.3 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | -1.26 | 3.18 | 15 | 2.88 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 13 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | 1.61 | 112 | 10 | 121 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | N2M | | 1.21 | 409 | 15 | 446 | 415 | 409 | 21 | 5.1 | 13 |
| B | µg/l | A1M | | -1.66 | 18.3 | 25 | 14.5 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | N2M | | -1.01 | 28.4 | 25 | 24.8 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -0.42 | 9.50 | 10 | 9.30 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | N2M | | -0.30 | 26.5 | 10 | 26.1 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | | 0.33 | 15 | *<0.7* | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | N2M | | | 0.51 | 15 | *<0.7* | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -0.74 | 1.35 | 10 | 1.30 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | N2M | | 112.45 | 1.06 | 15 | 10.00 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | 0.28 | 2.35 | 15 | 2.40 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | N2M | | 0.37 | 1.46 | 15 | 1.50 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | -0.65 | 21.5 | 10 | 20.8 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | N2M | | 0.00 | 6.00 | 15 | 6.00 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -1.11 | 77.5 | 10 | 73.2 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | N2M | | -0.73 | 247 | 10 | 238 | 248 | 247 | 8 | 3.2 | 14 |
| Mn | µg/l | A1M | | -0.51 | 19.5 | 10 | 19.0 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | N2M | | -0.58 | 3.66 | 15 | 3.50 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | -0.56 | 21.5 | 10 | 20.9 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | N2M | | -0.13 | 10.2 | 15 | 10.1 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | 0.24 | 3.36 | 10 | 3.40 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | N2M | | | 1.13 | 10 | <2 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -0.58 | 7.21 | 10 | 7.00 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | N2M | | -0.15 | 5.26 | 15 | 5.20 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Ti | µg/l | A1M | | -1.35 | 13.3 | 10 | 12.4 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | N2M | | 0.76 | 11.9 | 20 | 12.8 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| V | µg/l | A1M | | -1.99 | 7.33 | 10 | 6.60 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | N2M | | -0.68 | 1.58 | 15 | 1.50 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | 0.43 | 23.3 | 10 | 23.8 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | N2M | | | 3.18 | 15 | <5 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 14 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Al | µg/l | G3M | | -1.05 | 91.7 | 15 | 84.5 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.36 | 409 | 15 | 420 | 415 | 409 | 21 | 5.1 | 13 |
| Fe | µg/l | G3M | | -0.14 | 66.4 | 15 | 65.7 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.65 | 247 | 10 | 255 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | G3Hg | | -0.07 | 0.039 | 30 | 0.039 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | -0.04 | 0.075 | 25 | 0.075 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | G3M | | 0.45 | 29.5 | 15 | 30.5 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 1.38 | 3.66 | 15 | 4.04 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |

| Participant 15 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Al | µg/l | A1M | | 1.25 | 112 | 10 | 119 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | 0.45 | 91.7 | 15 | 94.8 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.36 | 409 | 15 | 420 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -1.19 | 7.25 | 10 | 6.82 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | 0.58 | 5.17 | 10 | 5.32 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 0.35 | 0.57 | 10 | 0.58 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | 0.00 | 18.3 | 25 | 18.3 | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | 0.27 | 38.9 | 25 | 40.2 | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | 0.20 | 28.4 | 25 | 29.1 | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -0.19 | 9.50 | 10 | 9.41 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | 0.73 | 8.44 | 15 | 8.90 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | 1.06 | 26.5 | 10 | 27.9 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | -0.81 | 0.33 | 15 | 0.31 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | 0.40 | 0.33 | 15 | 0.34 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | 0.00 | 0.51 | 15 | 0.51 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -0.15 | 1.35 | 10 | 1.34 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | 0.92 | 2.04 | 15 | 2.18 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | 0.63 | 1.06 | 15 | 1.11 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | 0.11 | 2.35 | 15 | 2.37 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | 0.17 | 3.12 | 15 | 3.16 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | 0.18 | 1.46 | 15 | 1.48 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |
| Cu | µg/l | A1M | | 0.00 | 21.5 | 10 | 21.5 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | 0.91 | 24.9 | 15 | 26.6 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | 0.42 | 6.00 | 15 | 6.19 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -0.54 | 77.5 | 10 | 75.4 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | 0.56 | 66.4 | 15 | 69.2 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.89 | 247 | 10 | 258 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | -0.80 | 0.12 | 25 | 0.11 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | -2.56 | 0.039 | 30 | 0.024 | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | -1.39 | 0.075 | 25 | 0.062 | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | 0.10 | 19.5 | 10 | 19.6 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | 1.08 | 29.5 | 15 | 31.9 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | 0.87 | 3.66 | 15 | 3.90 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | 0.19 | 21.5 | 10 | 21.7 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | 1.13 | 16.5 | 15 | 17.9 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | 0.92 | 10.2 | 15 | 10.9 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |

| Participant 15 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Ni | µg/l | A1M | | -0.42 | 3.36 | 10 | 3.29 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | 1.40 | 5.72 | 10 | 6.12 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | 0.71 | 1.13 | 10 | 1.17 | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -0.36 | 7.21 | 10 | 7.08 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -0.43 | 2.79 | 15 | 2.70 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -0.38 | 5.26 | 15 | 5.11 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | -0.41 | 4.35 | 10 | 4.26 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | 0.10 | 2.01 | 10 | 2.02 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | 0.08 | 4.91 | 10 | 4.93 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | -0.19 | 2.75 | 15 | 2.71 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | 0.85 | 1.56 | 15 | 1.66 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | -0.15 | 2.61 | 15 | 2.58 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | A1M | | -0.11 | 35.5 | 10 | 35.3 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | 1.20 | 100 | 10 | 106 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | 1.06 | 43.3 | 10 | 45.6 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| U | µg/l | A1M | | 0.03 | 6.30 | 10 | 6.31 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | 0.38 | 1.85 | 20 | 1.92 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | 0.70 | 4.37 | 15 | 4.60 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -0.25 | 7.33 | 10 | 7.24 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | 0.15 | 3.67 | 15 | 3.71 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | 0.34 | 1.58 | 15 | 1.62 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | -0.17 | 23.3 | 10 | 23.1 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | 0.21 | 28.5 | 20 | 29.1 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | 0.21 | 3.18 | 15 | 3.23 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

| Participant 17 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Al | µg/l | A1M | | -0.36 | 112 | 10 | 110 | 113 | 113 | 6 | 5.0 | 11 |
| | µg/l | G3M | | -0.13 | 91.7 | 15 | 90.8 | 91.1 | 91.7 | 4.8 | 5.2 | 11 |
| | µg/l | N2M | | 0.20 | 409 | 15 | 415 | 415 | 409 | 21 | 5.1 | 13 |
| As | µg/l | A1M | | -0.99 | 7.25 | 10 | 6.89 | 6.94 | 6.95 | 0.20 | 2.8 | 10 |
| | µg/l | G3M | | -0.31 | 5.17 | 10 | 5.09 | 5.20 | 5.17 | 0.12 | 2.3 | 10 |
| | µg/l | N2M | | 0.35 | 0.57 | 10 | 0.58 | 0.58 | 0.57 | 0.01 | 2.5 | 10 |
| B | µg/l | A1M | | | 18.3 | 25 | *< 200* | 18.3 | 18.2 | 1.9 | 10.4 | 7 |
| | µg/l | G3M | | | 38.9 | 25 | *< 200* | 38.9 | 38.9 | 2.3 | 6.0 | 6 |
| | µg/l | N2M | | | 28.4 | 25 | *< 200* | 28.4 | 28.2 | 2.1 | 7.5 | 6 |
| Ba | µg/l | A1M | | -1.83 | 9.50 | 10 | 8.63 | 9.20 | 9.21 | 0.32 | 3.5 | 11 |
| | µg/l | G3M | | -0.57 | 8.44 | 15 | 8.08 | 8.37 | 8.44 | 0.27 | 3.2 | 10 |
| | µg/l | N2M | | -0.68 | 26.5 | 10 | 25.6 | 26.1 | 26.5 | 0.9 | 3.3 | 11 |
| Cd | µg/l | A1M | | -0.40 | 0.33 | 15 | 0.32 | 0.32 | 0.32 | 0.01 | 3.5 | 9 |
| | µg/l | G3M | | -0.81 | 0.33 | 15 | 0.31 | 0.33 | 0.32 | 0.02 | 5.8 | 9 |
| | µg/l | N2M | | -0.26 | 0.51 | 15 | 0.50 | 0.51 | 0.51 | 0.02 | 3.0 | 9 |
| Co | µg/l | A1M | | -1.63 | 1.35 | 10 | 1.24 | 1.31 | 1.31 | 0.05 | 4.1 | 10 |
| | µg/l | G3M | | -0.65 | 2.04 | 15 | 1.94 | 2.00 | 2.04 | 0.09 | 4.6 | 9 |
| | µg/l | N2M | | -0.88 | 1.06 | 15 | 0.99 | 1.06 | 1.05 | 0.05 | 4.7 | 9 |
| Cr | µg/l | A1M | | -0.45 | 2.35 | 15 | 2.27 | 2.36 | 2.35 | 0.09 | 3.7 | 11 |
| | µg/l | G3M | | -0.04 | 3.12 | 15 | 3.11 | 3.11 | 3.12 | 0.10 | 3.1 | 10 |
| | µg/l | N2M | | 0.00 | 1.46 | 15 | 1.46 | 1.46 | 1.46 | 0.04 | 2.9 | 11 |

| Participant 17 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Cu | µg/l | A1M | | -0.09 | 21.5 | 10 | 21.4 | 21.2 | 21.4 | 0.7 | 3.0 | 11 |
| | µg/l | G3M | | 0.27 | 24.9 | 15 | 25.4 | 25.1 | 24.9 | 1.2 | 4.8 | 12 |
| | µg/l | N2M | | -0.13 | 6.00 | 15 | 5.94 | 6.00 | 5.98 | 0.14 | 2.4 | 11 |
| Fe | µg/l | A1M | | -0.93 | 77.5 | 10 | 73.9 | 74.7 | 75.1 | 4.9 | 6.5 | 12 |
| | µg/l | G3M | | -0.44 | 66.4 | 15 | 64.2 | 66.9 | 66.4 | 2.5 | 3.8 | 12 |
| | µg/l | N2M | | 0.40 | 247 | 10 | 252 | 248 | 247 | 8 | 3.2 | 14 |
| Hg | µg/l | A1Hg | | -0.67 | 0.12 | 25 | 0.11 | 0.14 | 0.14 | 0.02 | 15.4 | 11 |
| | µg/l | G3Hg | | | 0.039 | 30 | *< 0.13* | 0.042 | 0.043 | 0.005 | 10.6 | 6 |
| | µg/l | N2Hg | | | 0.075 | 25 | *< 0.13* | 0.075 | 0.076 | 0.010 | 12.6 | 9 |
| Mn | µg/l | A1M | | -0.82 | 19.5 | 10 | 18.7 | 18.9 | 18.9 | 0.7 | 3.5 | 12 |
| | µg/l | G3M | | -0.32 | 29.5 | 15 | 28.8 | 29.0 | 29.5 | 1.8 | 6.1 | 12 |
| | µg/l | N2M | | -0.18 | 3.66 | 15 | 3.61 | 3.67 | 3.66 | 0.22 | 5.9 | 13 |
| Mo | µg/l | A1M | | -1.67 | 21.5 | 10 | 19.7 | 21.0 | 20.8 | 0.9 | 4.3 | 10 |
| | µg/l | G3M | | -0.40 | 16.5 | 15 | 16.0 | 16.0 | 16.5 | 1.0 | 6.2 | 9 |
| | µg/l | N2M | | -0.54 | 10.2 | 15 | 9.8 | 10.2 | 10.3 | 0.6 | 5.8 | 10 |
| Ni | µg/l | A1M | | -0.65 | 3.36 | 10 | 3.25 | 3.32 | 3.32 | 0.09 | 2.8 | 12 |
| | µg/l | G3M | | -0.07 | 5.72 | 10 | 5.70 | 5.70 | 5.72 | 0.26 | 4.6 | 11 |
| | µg/l | N2M | | | 1.13 | 10 | *< 3* | 1.14 | 1.13 | 0.04 | 3.6 | 9 |
| Pb | µg/l | A1M | | -0.44 | 7.21 | 10 | 7.05 | 7.01 | 6.97 | 0.20 | 2.9 | 10 |
| | µg/l | G3M | | -0.57 | 2.79 | 15 | 2.67 | 2.67 | 2.64 | 0.10 | 3.8 | 9 |
| | µg/l | N2M | | -0.56 | 5.26 | 15 | 5.04 | 5.07 | 5.01 | 0.18 | 3.6 | 10 |
| Sb | µg/l | A1M | | -1.52 | 4.35 | 10 | 4.02 | 4.24 | 4.23 | 0.11 | 2.7 | 8 |
| | µg/l | G3M | | -0.50 | 2.01 | 10 | 1.96 | 2.01 | 2.00 | 0.06 | 2.9 | 9 |
| | µg/l | N2M | | -0.45 | 4.91 | 10 | 4.80 | 4.91 | 4.85 | 0.19 | 3.9 | 9 |
| Se | µg/l | A1M | | 0.63 | 2.75 | 15 | 2.88 | 2.72 | 2.78 | 0.12 | 4.2 | 10 |
| | µg/l | G3M | | 0.26 | 1.56 | 15 | 1.59 | 1.59 | 1.56 | 0.09 | 5.6 | 10 |
| | µg/l | N2M | | 0.31 | 2.61 | 15 | 2.67 | 2.61 | 2.62 | 0.10 | 3.7 | 10 |
| Sr | µg/l | A1M | | 0.85 | 35.5 | 10 | 37.0 | 33.9 | 34.7 | 1.4 | 3.9 | 7 |
| | µg/l | G3M | | 0.20 | 100 | 10 | 101 | 100 | 100 | 3 | 2.7 | 8 |
| | µg/l | N2M | | 0.79 | 43.3 | 10 | 45.0 | 42.9 | 43.3 | 1.4 | 3.2 | 7 |
| Ti | µg/l | A1M | | -0.15 | 13.3 | 10 | 13.2 | 13.0 | 12.9 | 0.3 | 2.5 | 8 |
| | µg/l | G3M | | | 5.31 | 15 | *< 10* | 5.23 | 5.31 | 0.31 | 5.9 | 6 |
| | µg/l | N2M | | 0.84 | 11.9 | 20 | 12.9 | 11.9 | 11.7 | 1.0 | 8.2 | 8 |
| U | µg/l | A1M | | -1.87 | 6.30 | 10 | 5.71 | 5.88 | 5.93 | 0.28 | 4.7 | 10 |
| | µg/l | G3M | | -0.76 | 1.85 | 20 | 1.71 | 1.75 | 1.85 | 0.17 | 9.4 | 9 |
| | µg/l | N2M | | -0.49 | 4.37 | 15 | 4.21 | 4.26 | 4.37 | 0.25 | 5.7 | 9 |
| V | µg/l | A1M | | -1.50 | 7.33 | 10 | 6.78 | 7.24 | 7.11 | 0.28 | 3.9 | 10 |
| | µg/l | G3M | | -0.54 | 3.67 | 15 | 3.52 | 3.62 | 3.67 | 0.20 | 5.5 | 9 |
| | µg/l | N2M | | -0.25 | 1.58 | 15 | 1.55 | 1.56 | 1.58 | 0.06 | 3.7 | 9 |
| Zn | µg/l | A1M | | 0.69 | 23.3 | 10 | 24.1 | 23.7 | 23.5 | 1.0 | 4.4 | 11 |
| | µg/l | G3M | | -0.14 | 28.5 | 20 | 28.1 | 28.5 | 28.7 | 3.3 | 11.4 | 10 |
| | µg/l | N2M | | 8.43 | 3.18 | 15 | 5.19 | 3.18 | 3.20 | 0.24 | 7.4 | 8 |

# APPENDIX 8: Summary of the z scores

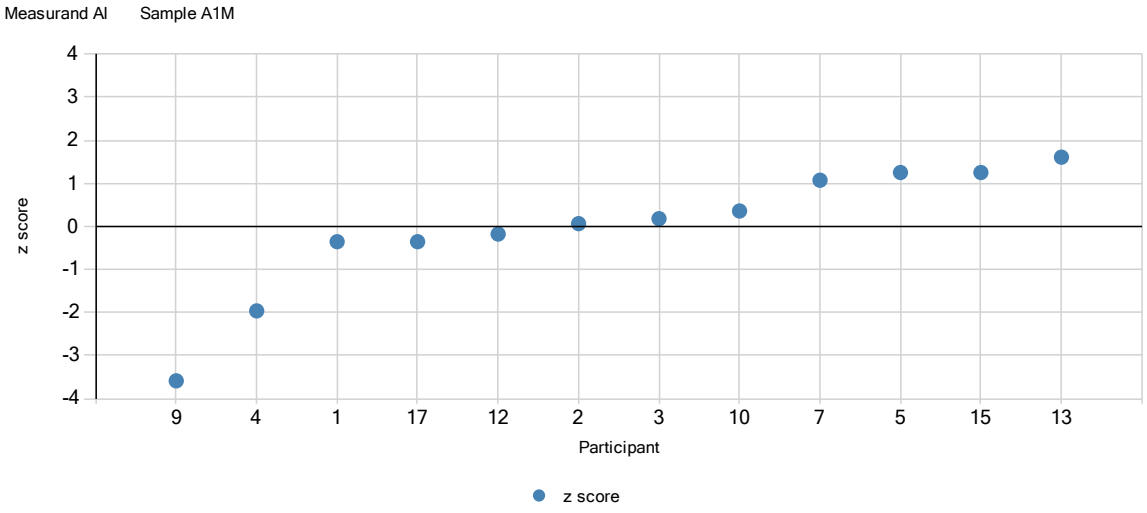
| Measurand | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 17 | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | A1M | S | S | S | S | S | . | S | . | u | S | . | S | S | . | S | S | 91.7 |
| | G3M | S | S | S | S | U | . | S | S | q | S | . | S | . | S | S | S | 84.6 |
| | N2M | S | S | S | S | u | . | S | S | S | S | . | S | S | S | S | S | 92.9 |
| As | A1M | S | S | S | . | S | . | S | . | S | S | . | S | . | . | S | S | 100 |
| | G3M | S | S | S | . | u | . | S | S | S | S | . | S | . | . | S | S | 90.9 |
| | N2M | S | S | S | . | U | . | S | S | S | S | . | S | . | . | S | S | 90.9 |
| B | A1M | . | u | S | S | S | . | S | . | u | . | . | S | S | . | S | . | 77.8 |
| | G3M | . | u | S | S | q | . | S | S | u | . | . | S | . | . | S | . | 66.7 |
| | N2M | . | u | S | S | Q | . | S | u | u | . | . | S | S | . | S | . | 60.0 |
| Ba | A1M | S | S | S | S | S | . | S | . | . | S | . | S | S | . | S | S | 100 |
| | G3M | S | S | S | S | U | . | S | S | . | S | . | S | . | . | S | S | 90.9 |
| | N2M | S | S | S | S | u | . | S | S | . | S | . | S | S | . | S | S | 91.7 |
| Cd | A1M | S | S | S | . | S | . | S | . | U | S | . | S | . | . | S | S | 90.0 |
| | G3M | S | S | S | . | U | . | S | S | U | S | . | S | . | . | S | S | 81.8 |
| | N2M | S | S | S | . | u | . | S | S | U | S | . | S | . | . | S | S | 81.8 |
| Co | A1M | S | S | S | . | S | . | S | . | . | S | . | S | S | . | S | S | 100 |
| | G3M | S | S | S | . | u | . | S | S | . | S | . | S | . | . | S | S | 90.0 |
| | N2M | S | S | S | . | U | . | S | S | . | S | . | S | U | . | S | S | 81.8 |
| Cr | A1M | S | S | S | . | S | . | S | . | S | S | . | S | S | . | S | S | 100 |
| | G3M | S | S | S | . | u | . | S | S | S | S | . | S | . | . | S | S | 90.9 |
| | N2M | S | S | S | . | U | . | S | S | S | S | . | S | S | . | S | S | 91.7 |
| Cu | A1M | S | S | S | S | S | . | S | . | u | S | . | S | S | . | S | S | 91.7 |
| | G3M | S | S | S | S | u | . | S | S | S | S | S | S | . | . | S | S | 92.3 |
| | N2M | S | S | S | S | U | . | S | S | S | S | . | S | S | . | S | S | 92.3 |
| Fe | A1M | S | S | S | S | S | . | S | . | u | S | . | S | S | . | S | S | 91.7 |
| | G3M | S | S | S | S | U | . | S | u | q | S | Q | S | . | S | S | S | 71.4 |
| | N2M | S | S | S | S | u | . | S | S | S | S | S | S | S | S | S | S | 93.3 |
| Hg | A1Hg | S | S | S | . | S | S | S | . | S | S | U | U | . | . | S | S | 83.3 |
| | G3Hg | . | S | S | . | U | U | S | . | S | S | U | U | . | S | q | . | 54.5 |
| | N2Hg | . | S | S | . | u | S | S | . | S | S | U | S | . | S | S | . | 81.8 |
| Mn | A1M | S | S | S | S | S | . | S | . | S | S | . | S | S | . | S | S | 100 |
| | G3M | S | S | S | S | u | . | S | u | S | S | S | S | . | S | S | S | 85.7 |
| | N2M | S | S | S | S | U | . | S | S | S | S | . | S | S | S | S | S | 92.9 |
| Mo | A1M | S | S | S | . | S | . | S | . | . | S | . | S | S | . | S | S | 100 |
| | G3M | S | S | S | . | u | . | S | S | . | S | . | S | . | . | S | S | 90.0 |
| | N2M | S | S | S | . | U | . | S | S | . | S | . | S | S | . | S | S | 90.9 |
| Ni | A1M | S | S | S | S | S | . | S | . | S | S | . | S | S | . | S | S | 100 |
| | G3M | S | S | S | S | u | . | S | S | S | S | . | S | . | . | S | S | 91.7 |
| | N2M | S | S | S | . | U | . | S | S | S | S | . | S | . | . | S | . | 90.0 |
| Pb | A1M | S | S | S | . | S | . | S | . | U | S | . | S | S | . | S | S | 90.9 |
| | G3M | S | S | S | . | U | . | S | S | Q | S | . | S | . | . | S | S | 81.8 |
| | N2M | S | S | S | . | u | . | S | S | Q | S | . | S | S | . | S | S | 83.3 |
| Sb | A1M | S | S | S | . | S | . | S | . | U | U | . | S | . | . | S | S | 80.0 |
| | G3M | S | S | S | . | U | . | S | S | U | S | . | S | . | . | S | S | 81.8 |
| | N2M | S | S | S | . | u | . | S | S | U | S | . | S | . | . | S | S | 81.8 |

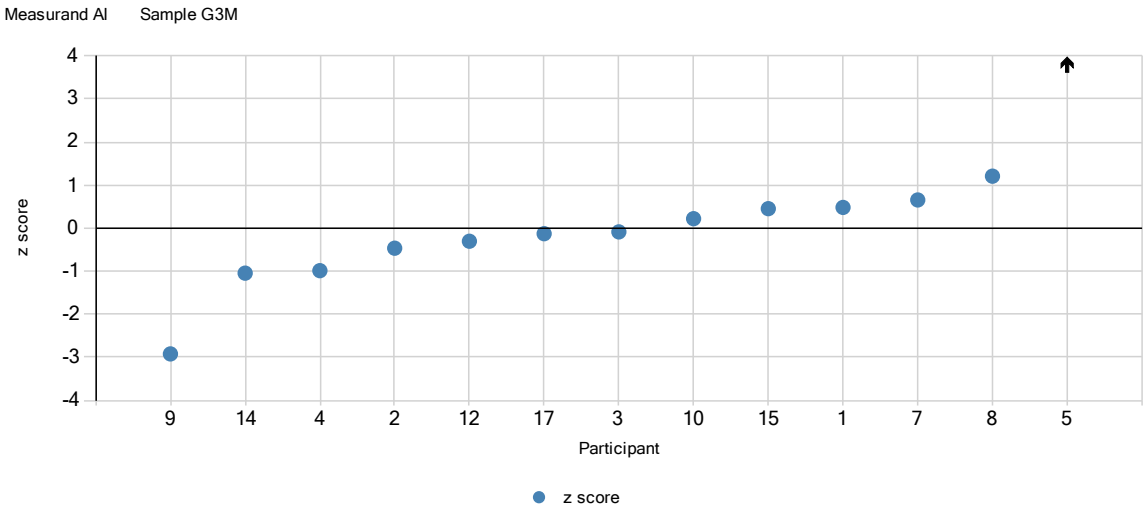
| Measurand | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 17 | % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Se | A1M | **S** | **S** | **S** | . | **S** | . | **S** | . | *S* | **S** | . | **S** | . | . | **S** | **S** | 100 |
| | G3M | **S** | **S** | **S** | . | **U** | . | **S** | *S* | *S* | **S** | . | **S** | . | . | **S** | **S** | 90.9 |
| | N2M | **S** | **S** | **S** | . | **u** | . | **S** | *S* | *S* | **S** | . | **S** | . | . | **S** | **S** | 90.9 |
| Sr | A1M | . | **S** | . | *U* | *S* | . | **S** | . | . | **S** | . | **S** | . | . | **S** | *S* | 87.5 |
| | G3M | . | **S** | . | *S* | *u* | . | **S** | *S* | . | **S** | . | **S** | . | . | **S** | *S* | 88.9 |
| | N2M | . | **S** | . | *Q* | *U* | . | **S** | *S* | . | **S** | . | **S** | . | . | **S** | *S* | 77.8 |
| Ti | A1M | *S* | **S** | . | . | *S* | . | **S** | . | . | *S* | . | **S** | *S* | . | . | *S* | 100 |
| | G3M | *S* | **S** | . | . | *U* | . | **S** | *S* | . | *S* | . | **S** | . | . | . | . | 85.7 |
| | N2M | *S* | **S** | . | . | *u* | . | **S** | *S* | . | *S* | . | **S** | *S* | . | . | *S* | 88.9 |
| U | A1M | **S** | **S** | **S** | . | **S** | . | **S** | . | *S* | **q** | . | **S** | . | . | **S** | **S** | 90.0 |
| | G3M | **S** | **S** | **S** | . | **U** | . | **S** | *q* | *Q* | **S** | . | **S** | . | . | **S** | **S** | 72.7 |
| | N2M | **S** | **S** | **S** | . | **u** | . | **S** | *S* | *U* | **S** | . | **S** | . | . | **S** | **S** | 81.8 |
| V | A1M | **S** | **S** | **S** | . | **S** | . | **S** | . | . | **S** | . | **S** | *S* | . | **S** | **S** | 100 |
| | G3M | **S** | **S** | **S** | . | **u** | . | **S** | *S* | . | **S** | . | **S** | . | . | **S** | **S** | 90.0 |
| | N2M | **S** | **S** | **S** | . | **U** | . | **S** | *u* | . | **S** | . | **S** | *S* | . | **S** | **S** | 81.8 |
| Zn | A1M | **S** | **S** | **S** | *S* | **S** | . | **S** | . | . | **S** | . | **S** | S | . | **S** | **S** | 100 |
| | G3M | **S** | **S** | **S** | *S* | **u** | . | **S** | *u* | . | **S** | **Q** | **S** | . | . | **S** | **S** | 75.0 |
| | N2M | **S** | **S** | **S** | *S* | **U** | . | **S** | *u* | . | **S** | . | **S** | . | . | **S** | **U** | 72.7 |
| % | | 100 | 95 | 100 | 92 | 33 | 67 | 100 | 83 | 55 | 97 | 38 | 97 | 96 | 100 | 98 | 98 | |
| accredited | | 52 | 63 | 54 | | 57 | 3 | 63 | | 15 | 57 | 8 | 61 | 15 | 8 | 57 | 51 | |

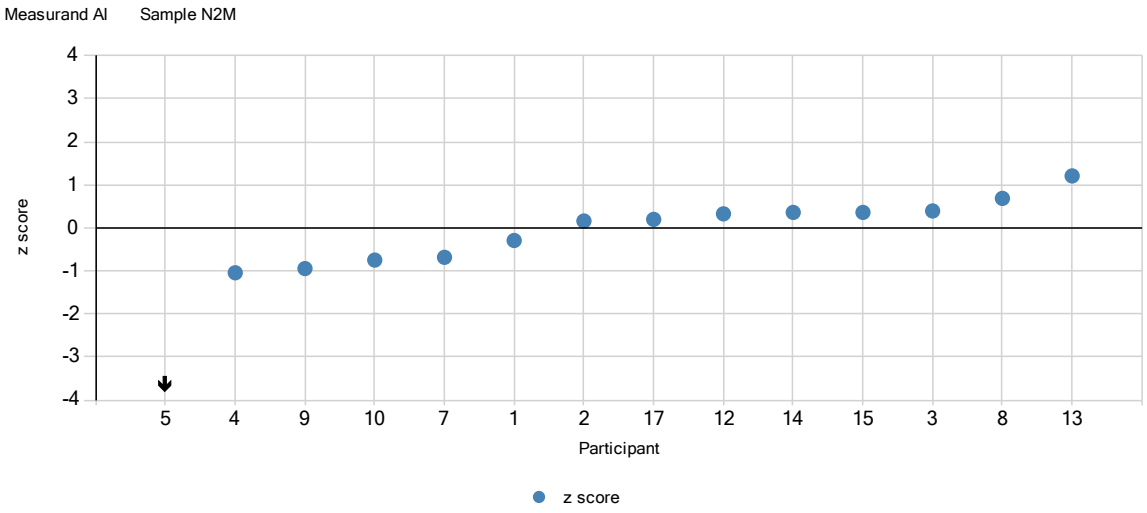
S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), and u - unsatisfactory ($z \leq -3$), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 88 % in accredited: 89 % in non-accredited: 80

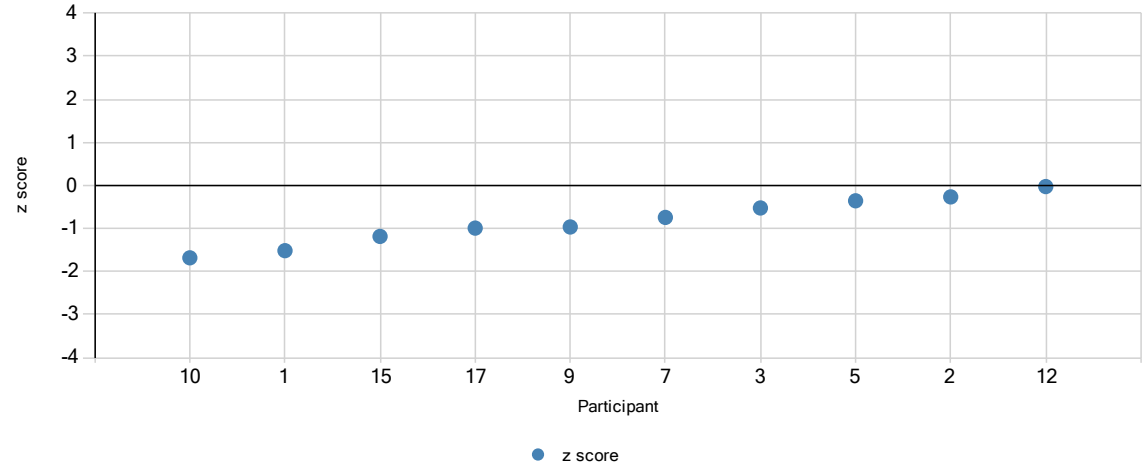
# APPENDIX 9: z scores in ascending order



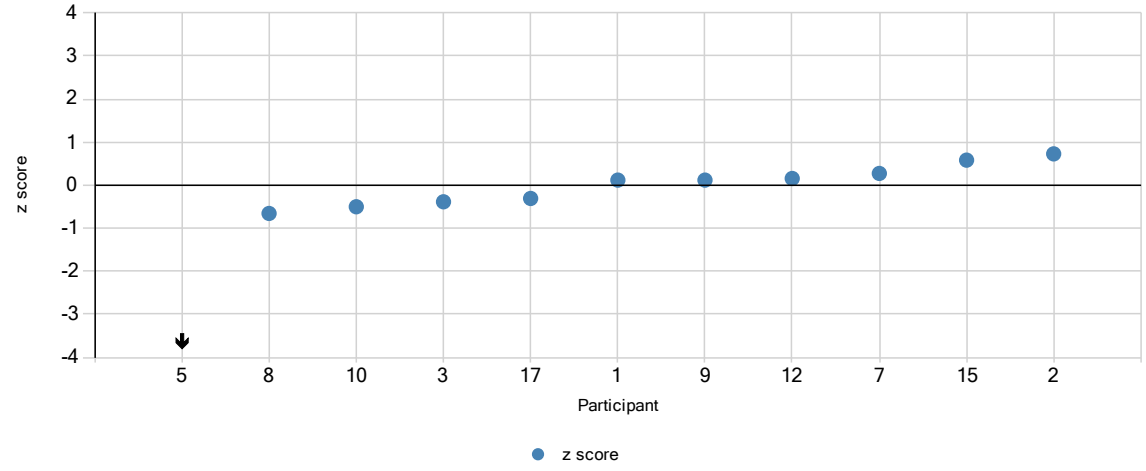



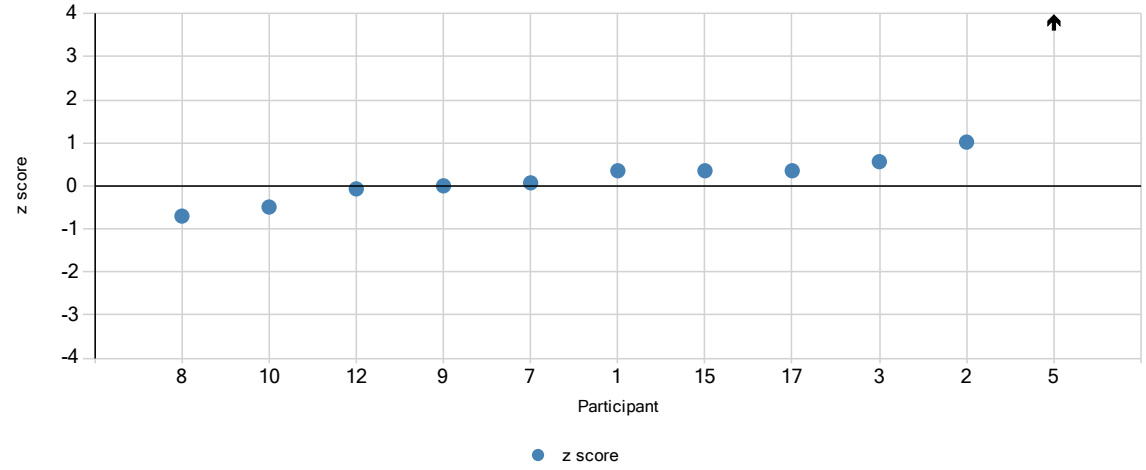
Measurand As Sample A1M

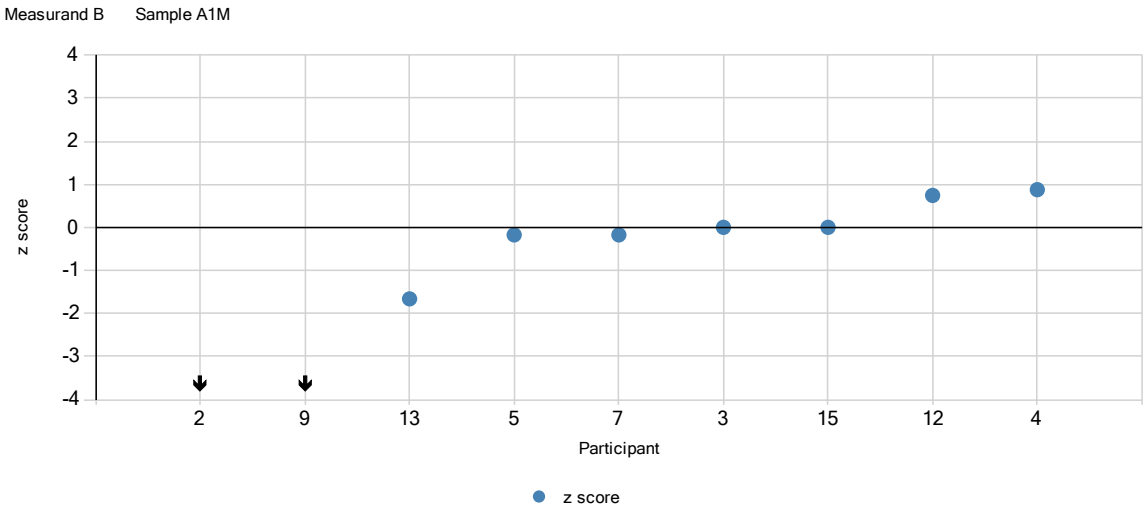


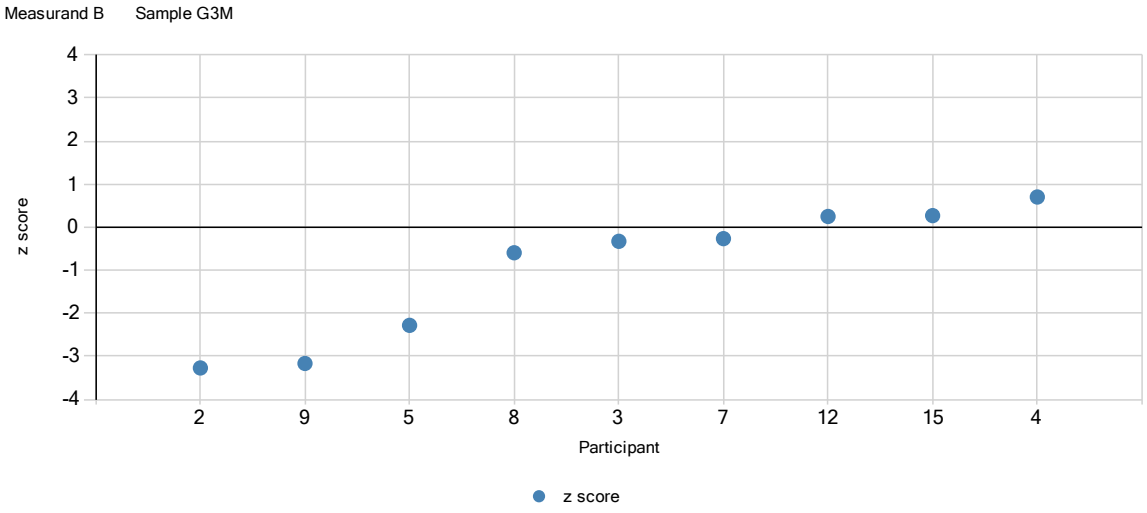

Measurand As Sample G3M

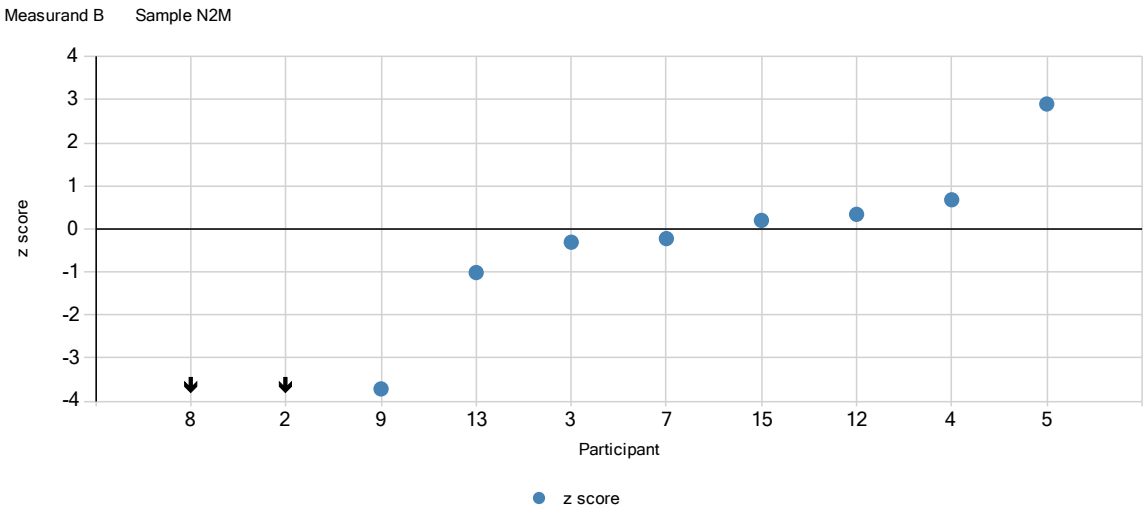



Measurand As Sample N2M

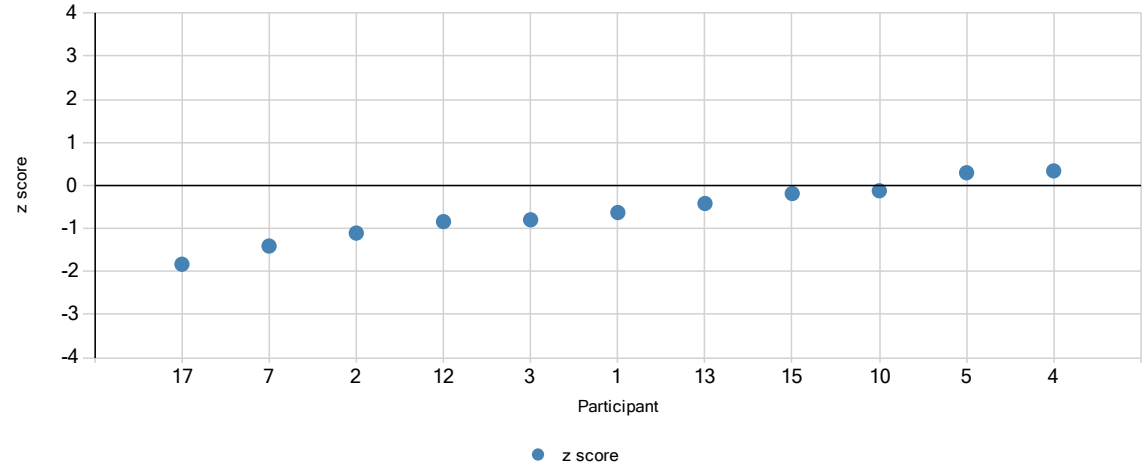



Measurand B
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
2
9
13
5
7
3
15
12
4
Participant
z score

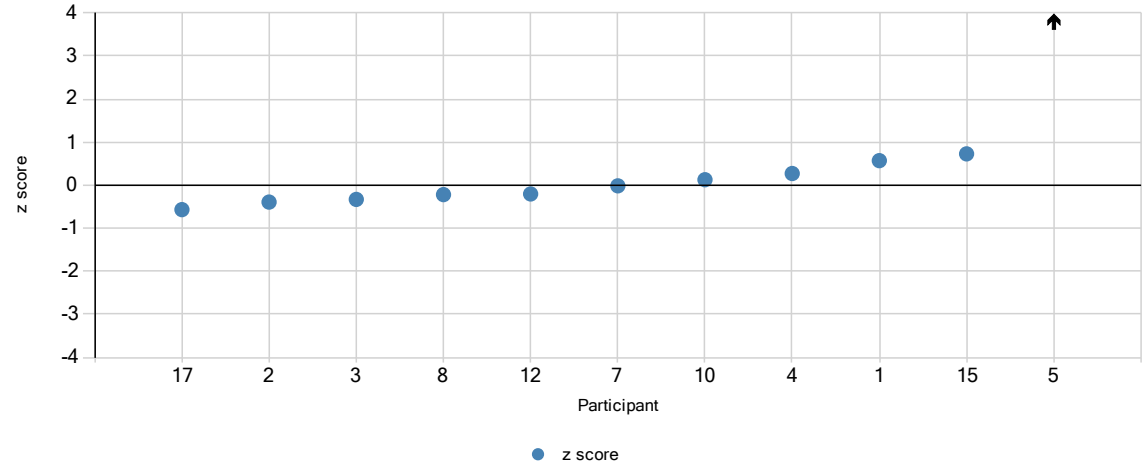

Measurand B
Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
2
9
5
8
3
7
12
15
4
Participant
z score


Measurand B
Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
8
2
9
13
3
7
15
12
4
5
Participant
z score

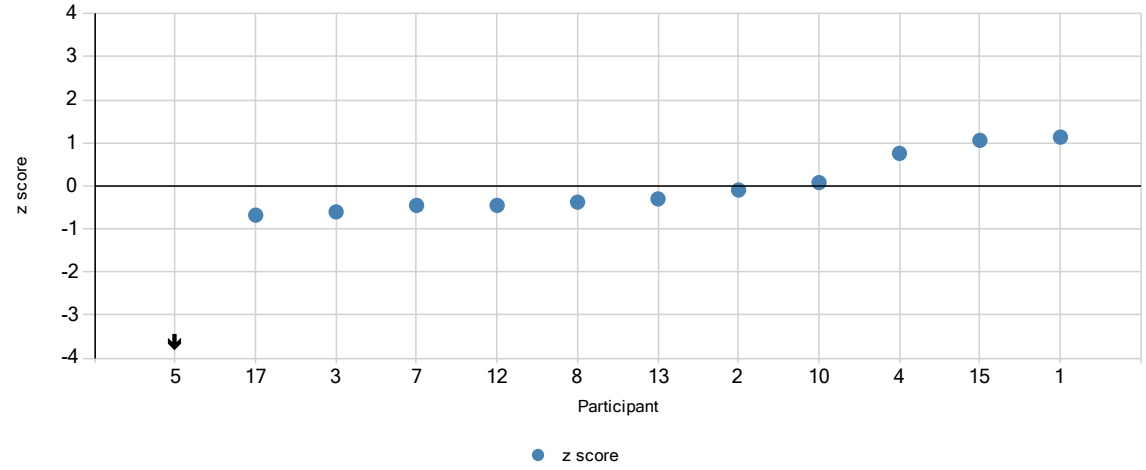
Measurand Ba Sample A1M

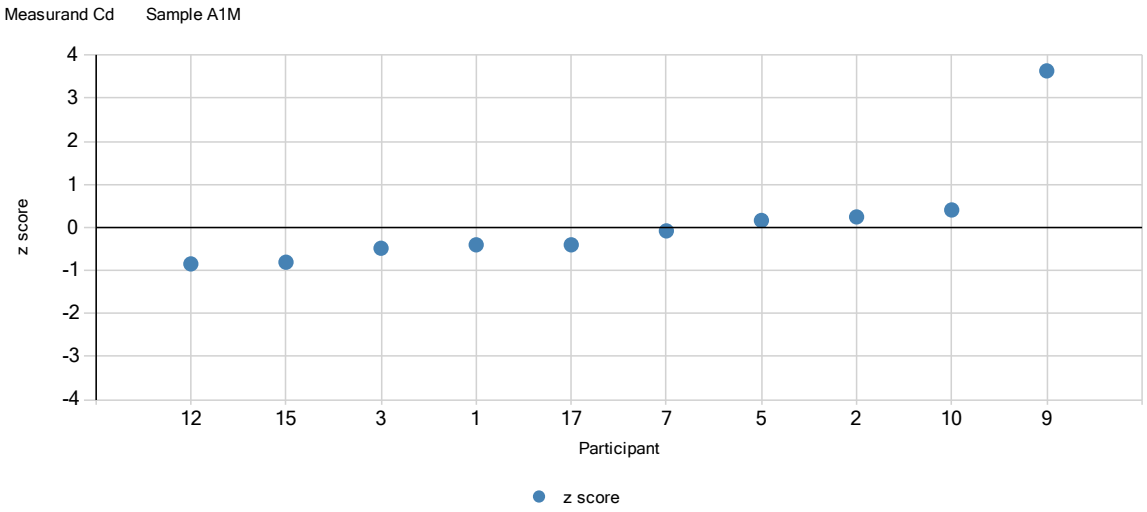


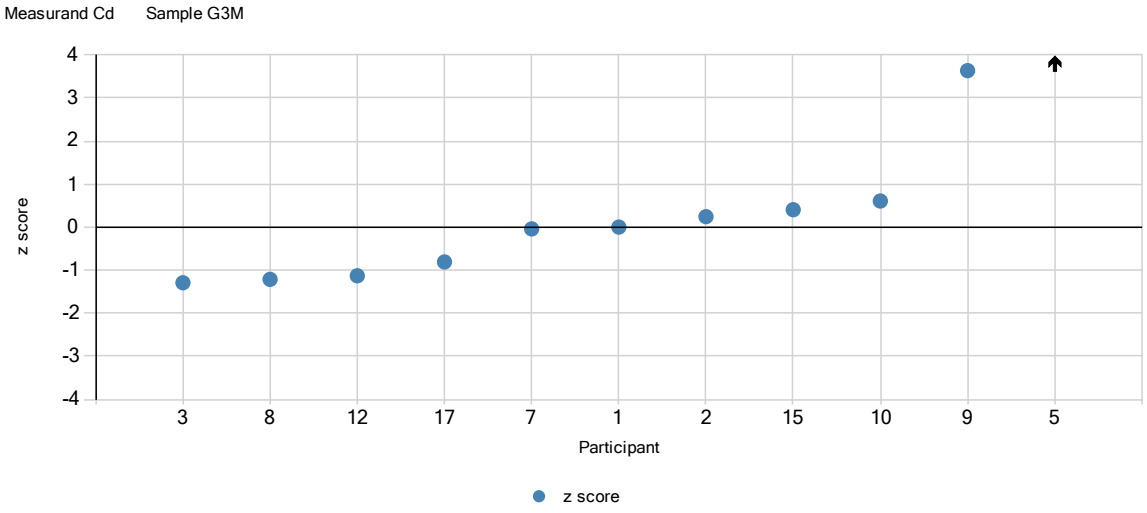

Measurand Ba Sample G3M

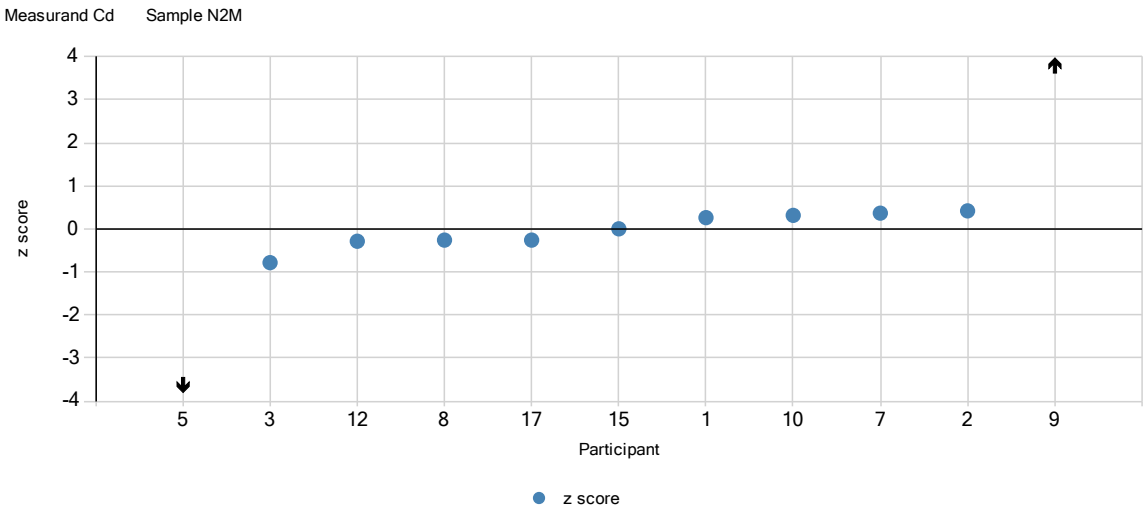



Measurand Ba Sample N2M

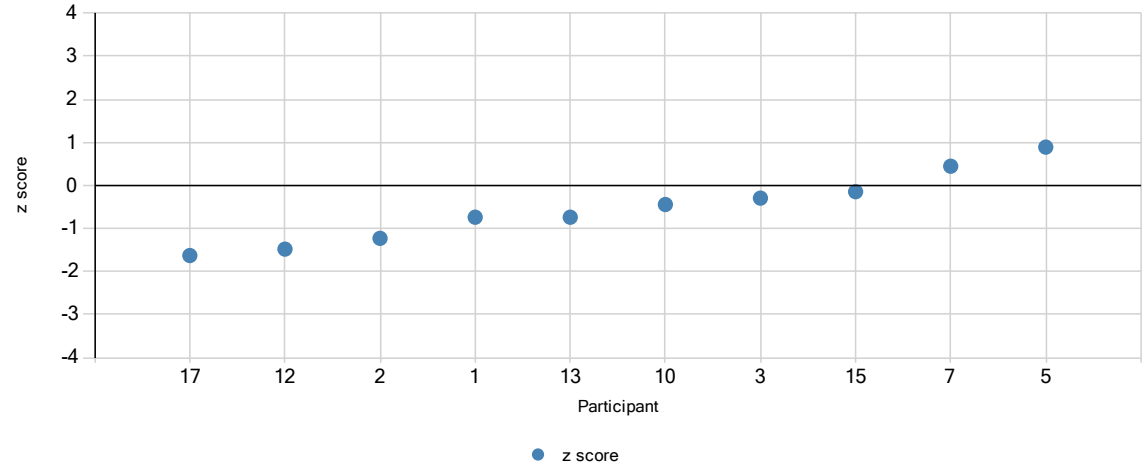



Measurand Cd Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
12 15 3 1 17 7 5 2 10 9
Participant
z score

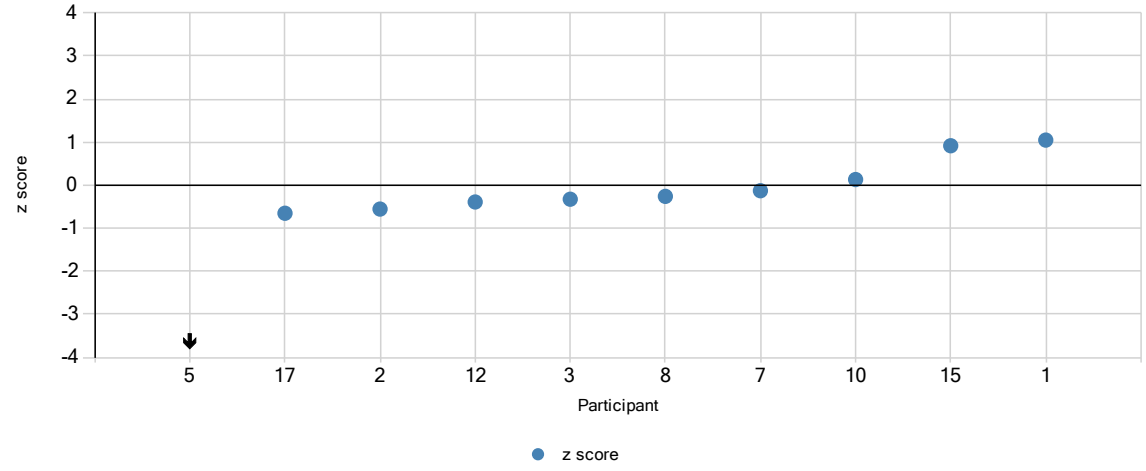

Measurand Cd Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
3 8 12 17 7 1 2 15 10 9 5
Participant
z score


Measurand Cd Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 3 12 8 17 15 1 10 7 2 9
Participant
z score

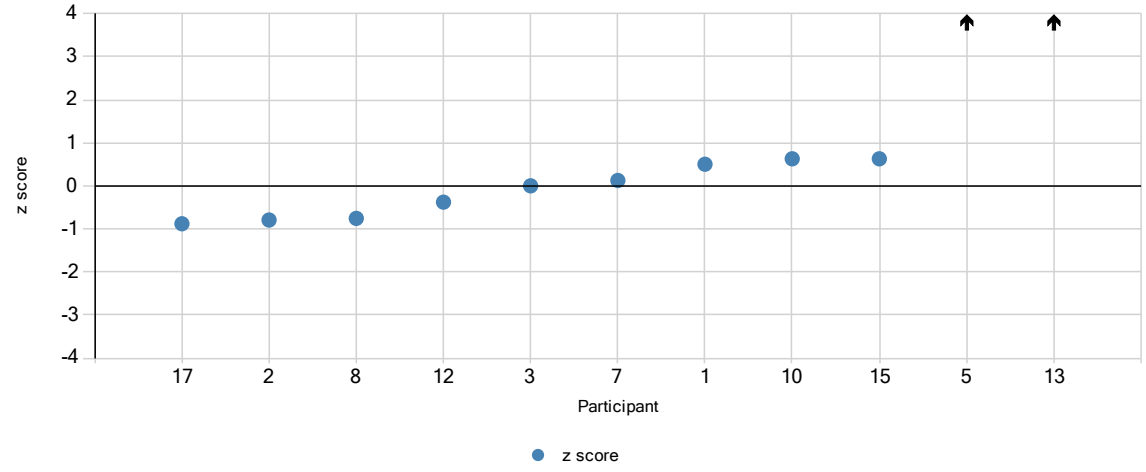
Measurand Co Sample A1M

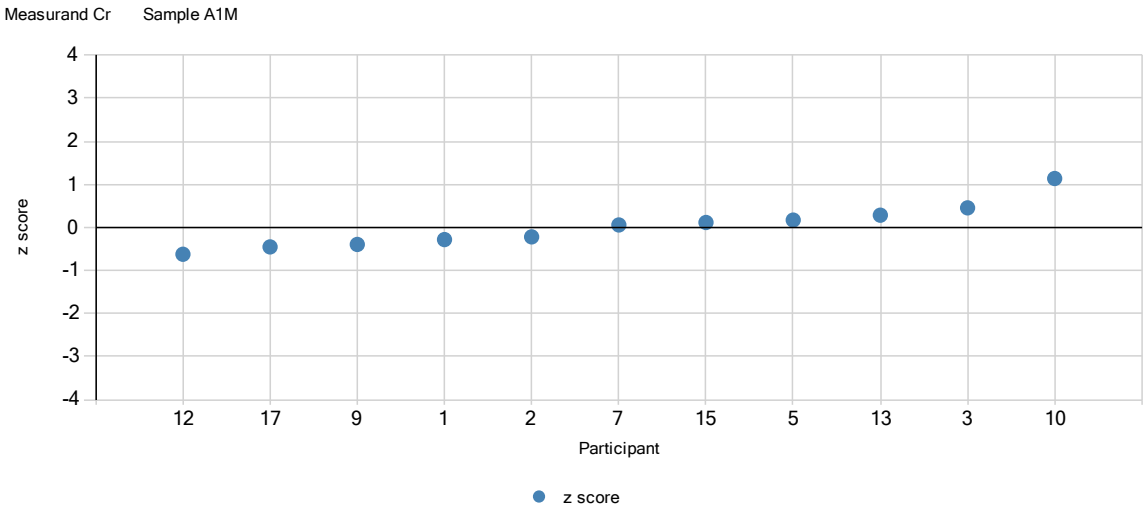


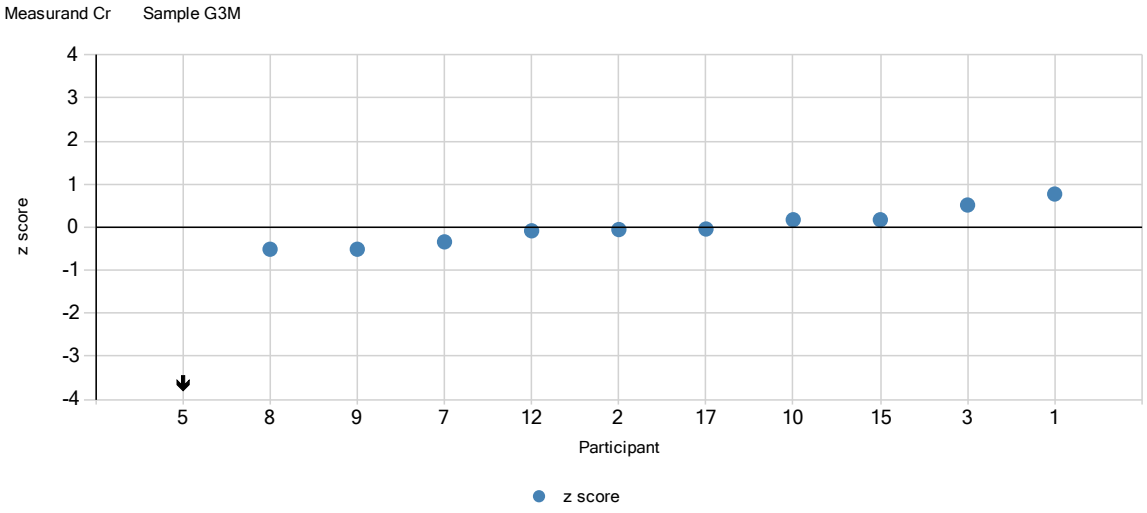

Measurand Co Sample G3M

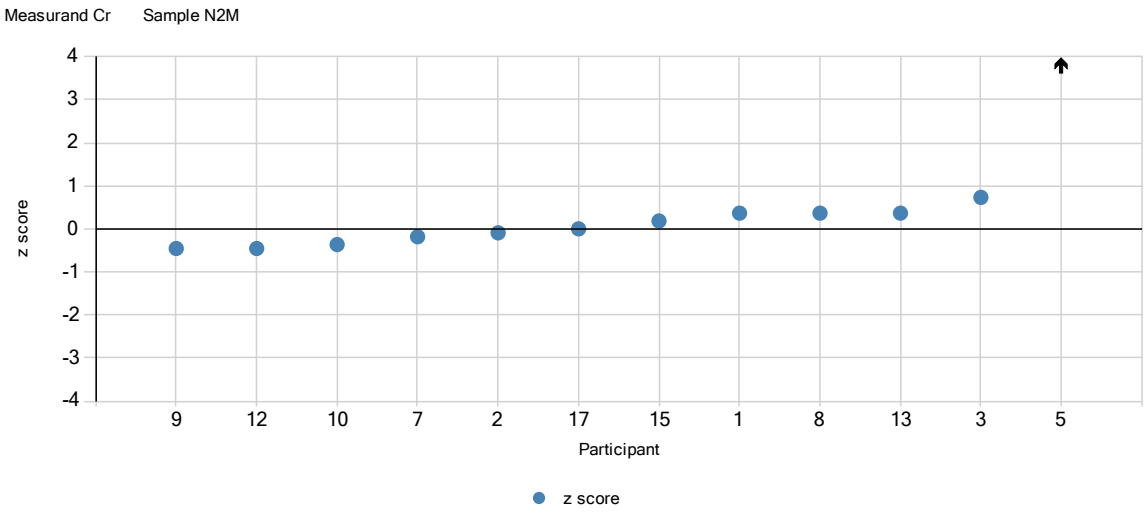



Measurand Co Sample N2M

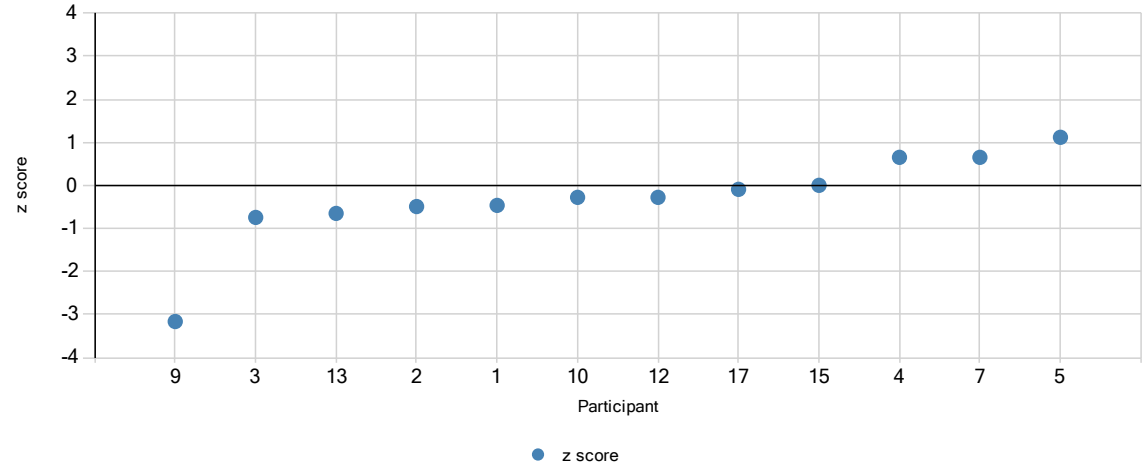



Measurand Cr
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
12
17
9
1
2
7
15
5
13
3
10
Participant
z score

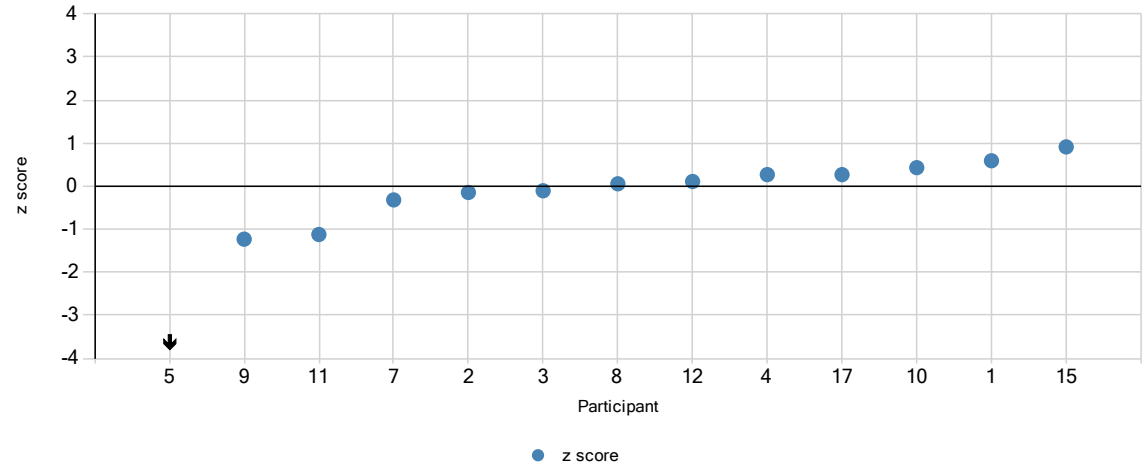

Measurand Cr
Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
5
8
9
7
12
2
17
10
15
3
1
Participant
z score


Measurand Cr
Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
9
12
10
7
2
17
15
1
8
13
3
5
Participant
z score

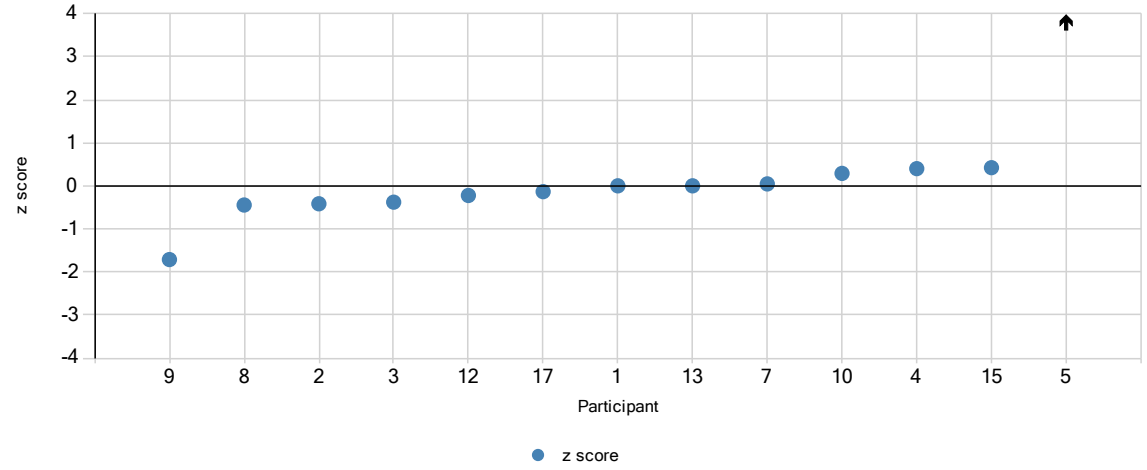
Measurand Cu Sample A1M

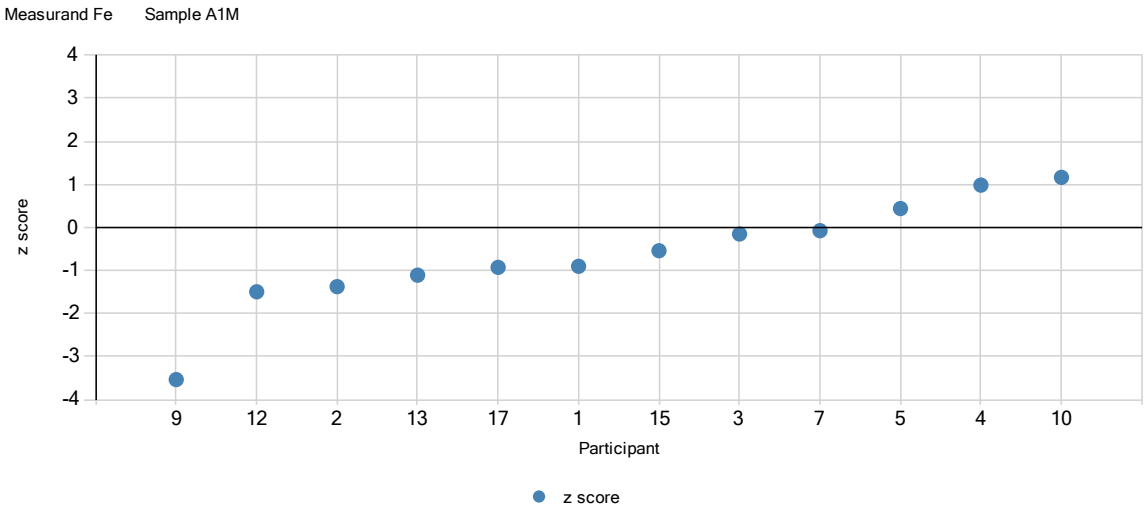


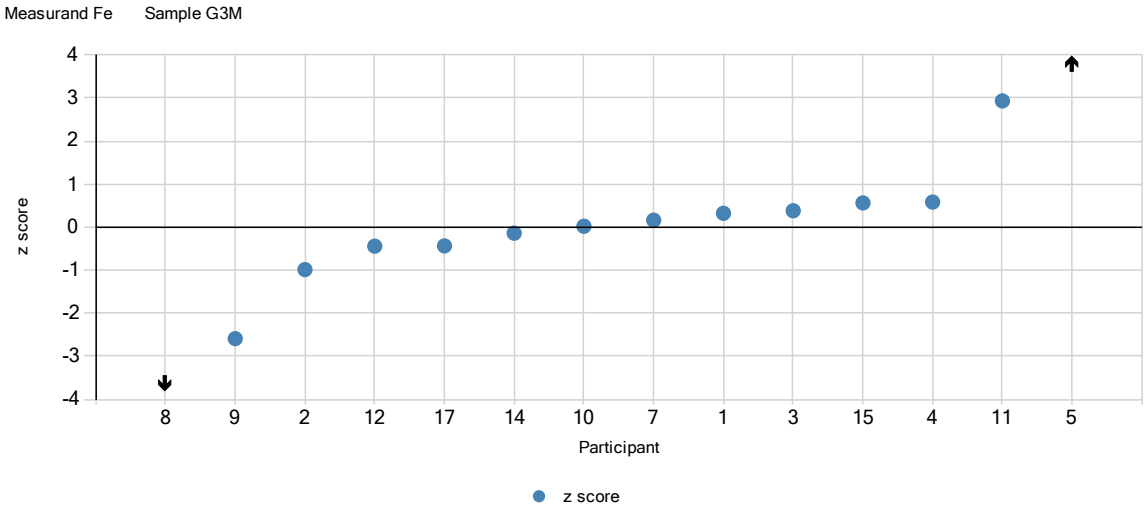

Measurand Cu Sample G3M

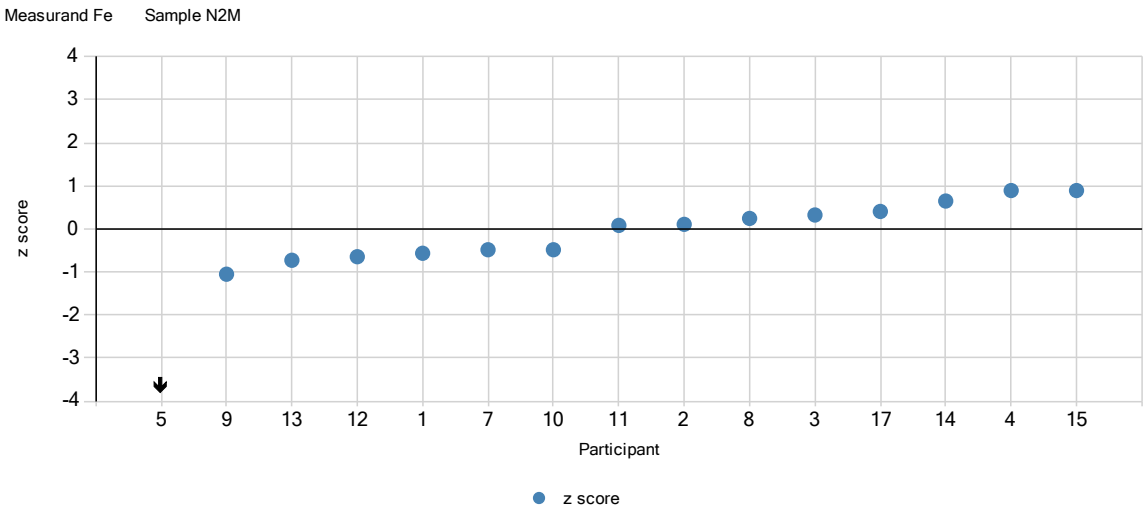



Measurand Cu Sample N2M

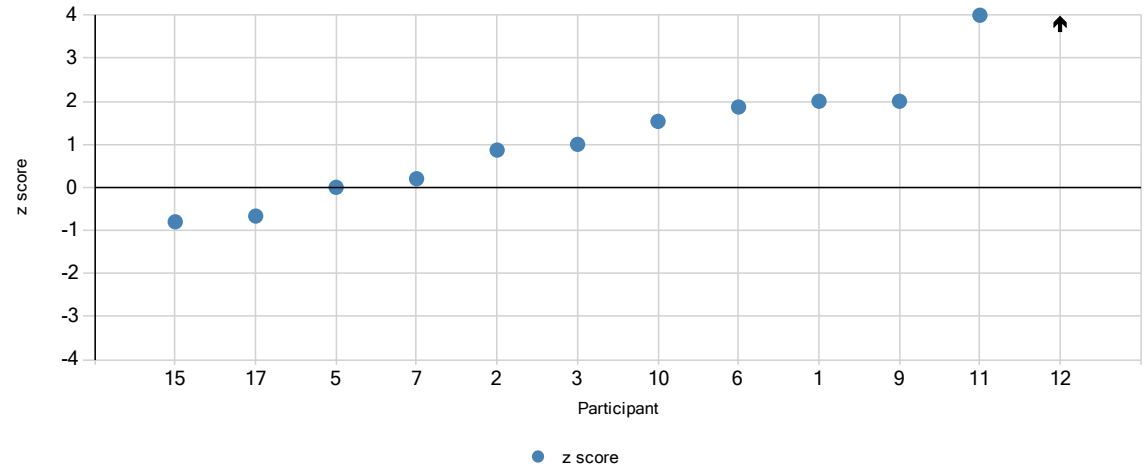



Measurand Fe Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
9 12 2 13 17 1 15 3 7 5 4 10
Participant
z score

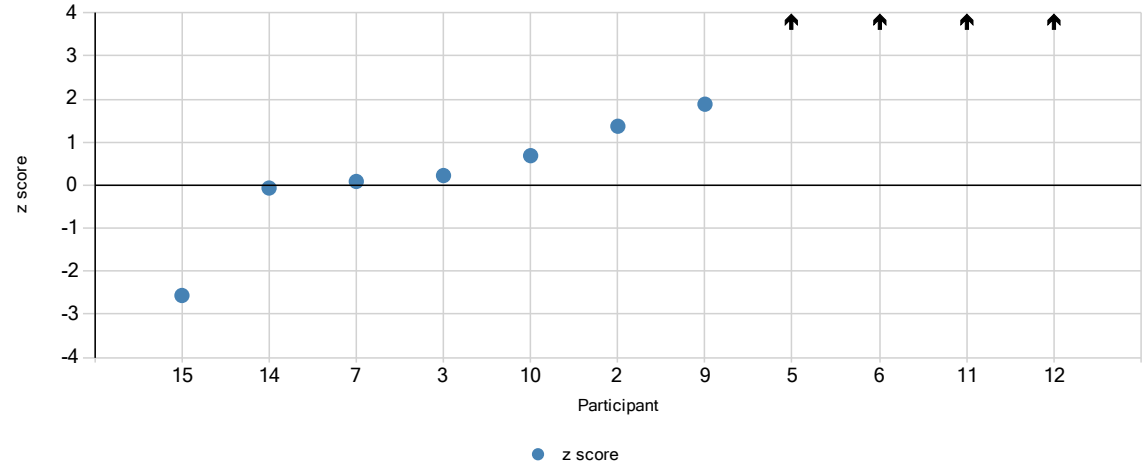

Measurand Fe Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
8 9 2 12 17 14 10 7 1 3 15 4 11 5
Participant
z score


Measurand Fe Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 9 13 12 1 7 10 11 2 8 3 17 14 4 15
Participant
z score

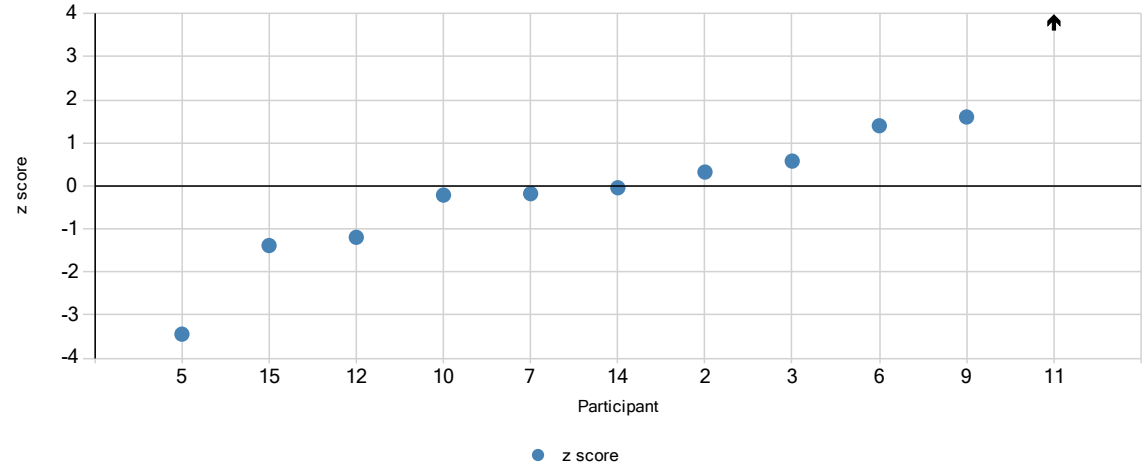
Measurand Hg Sample A1Hg

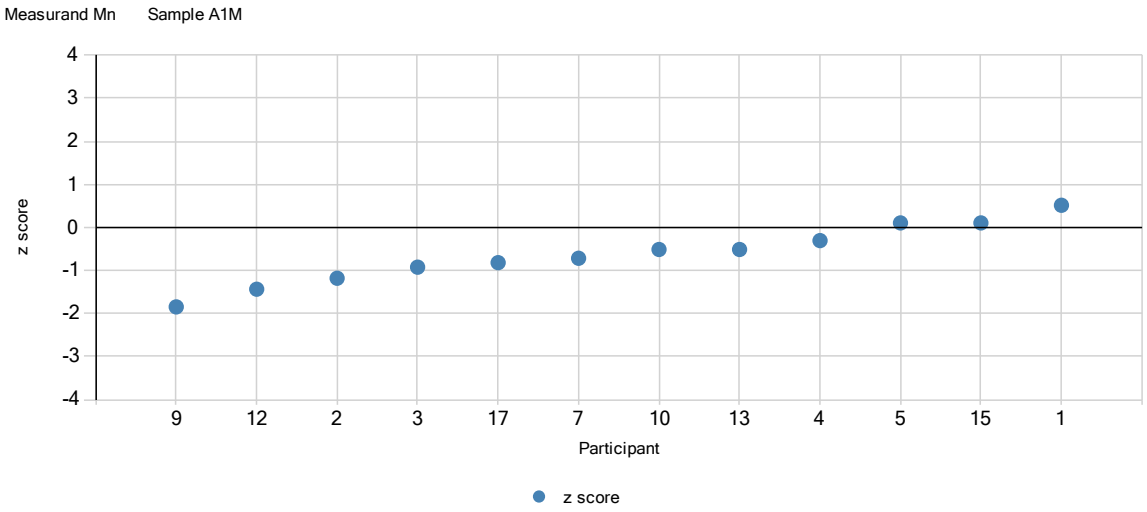



Measurand Hg Sample G3Hg




Measurand Hg Sample N2Hg




Measurand Mn Sample A1M
z score
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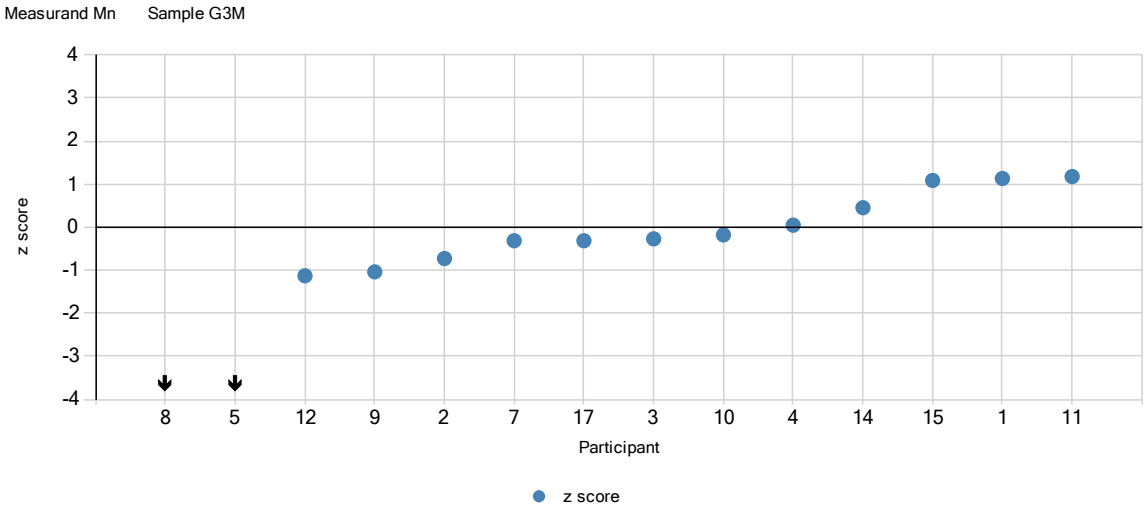
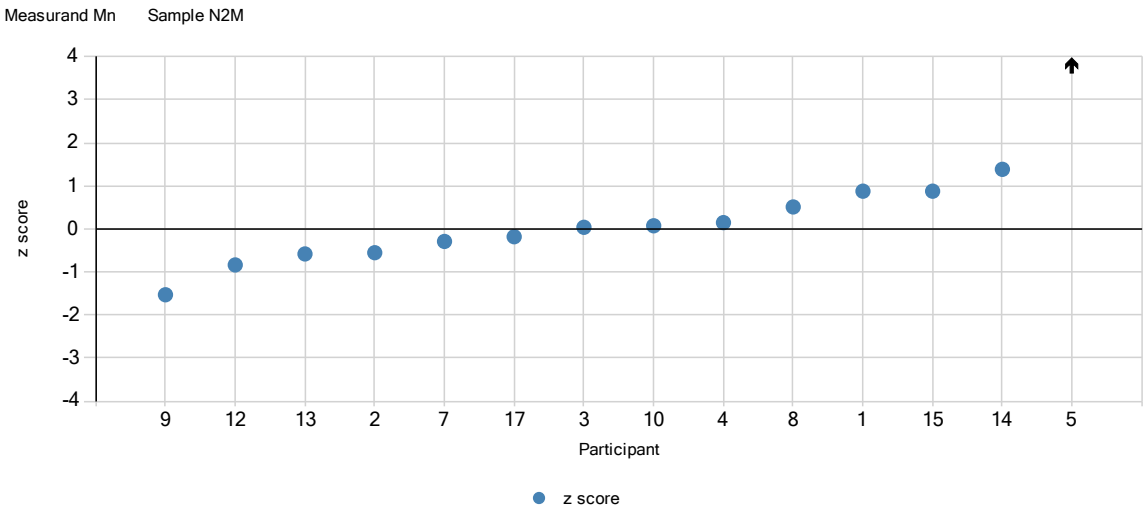
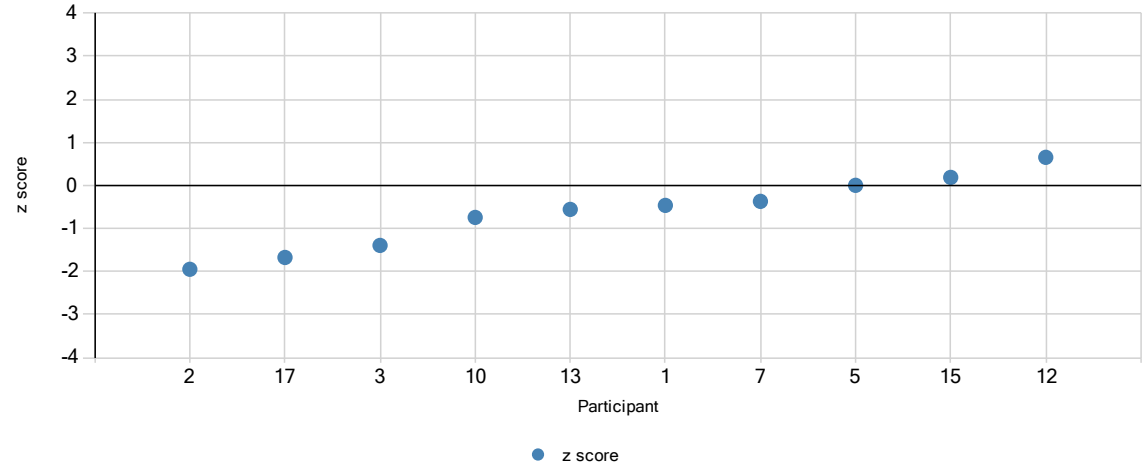
3
2
1
0
-1
-2
-3
-4
9 12 2 3 17 7 10 13 4 5 15 1
Participant
z score

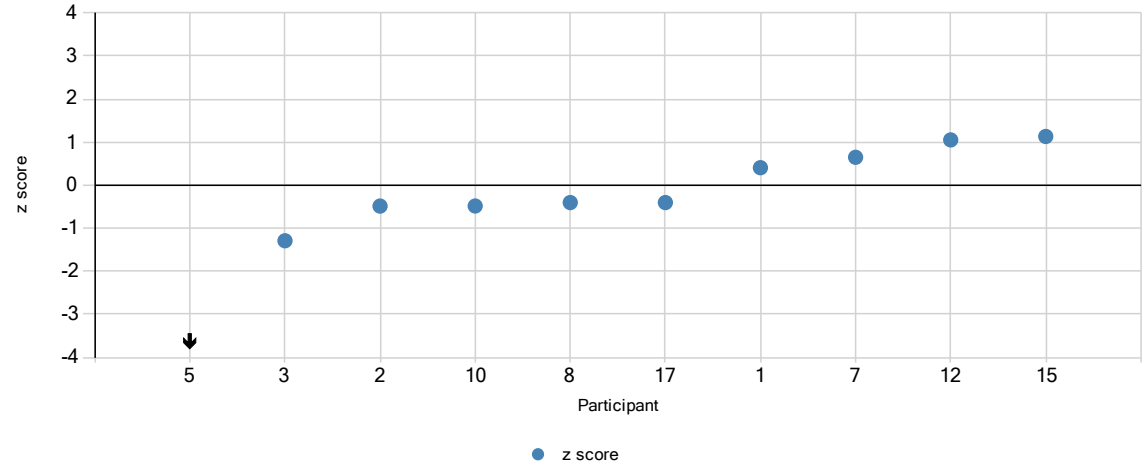

Measurand Mn Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
8 5 12 9 2 7 17 3 10 4 14 15 1 11
Participant
z score


Measurand Mn Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
9 12 13 2 7 17 3 10 4 8 1 15 14 5
Participant
z score

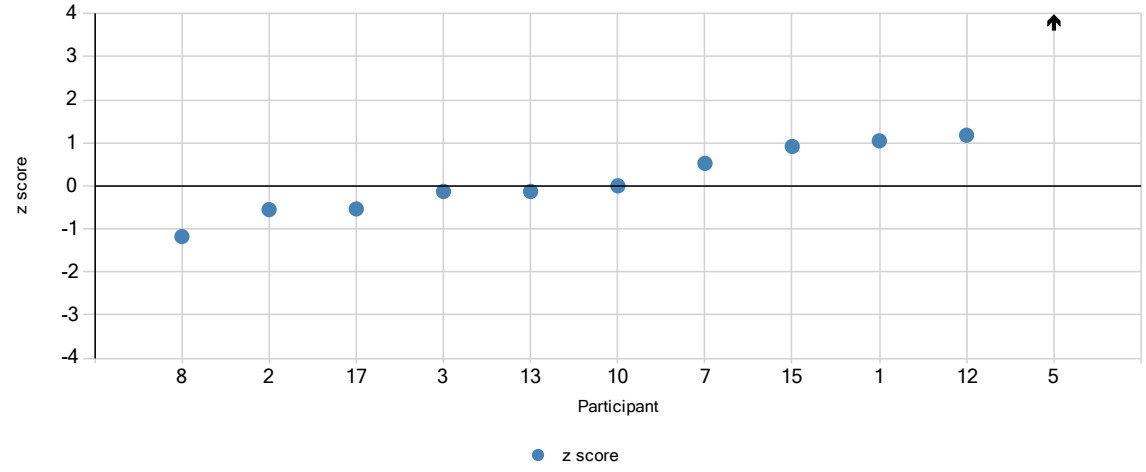
Measurand Mo Sample A1M

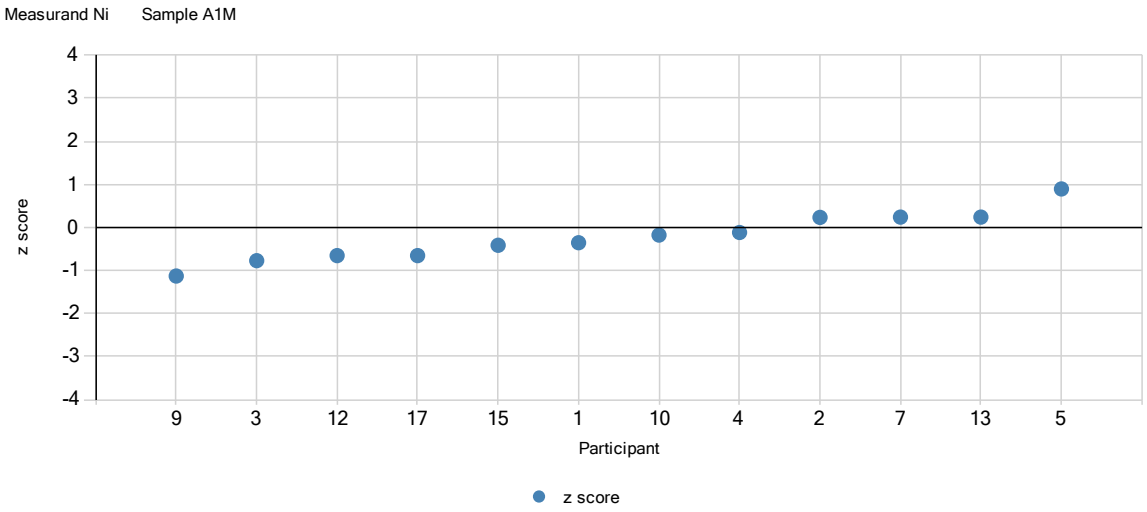



Measurand Mo Sample G3M




Measurand Mo Sample N2M




Measurand Ni Sample A1M
z score
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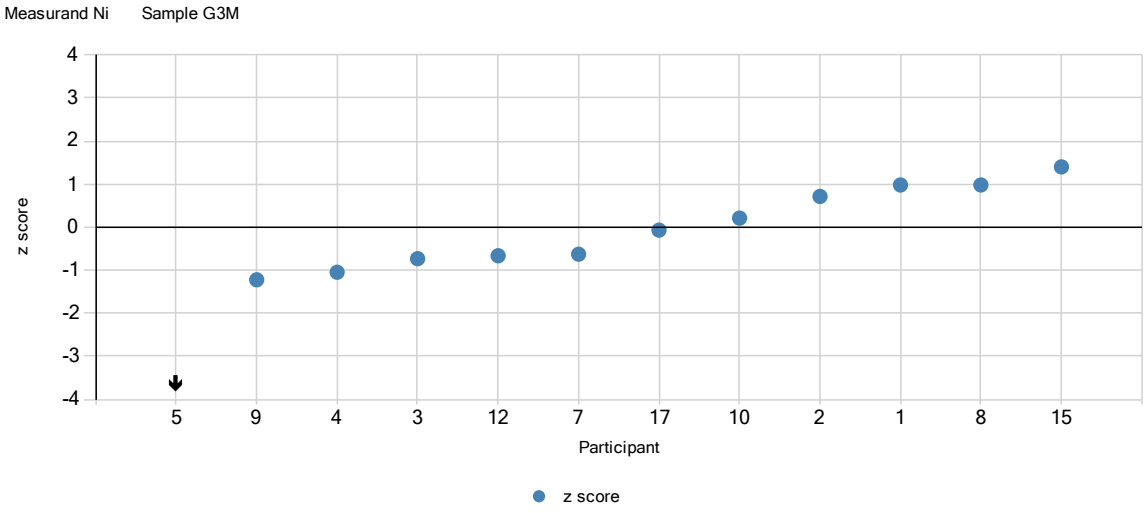
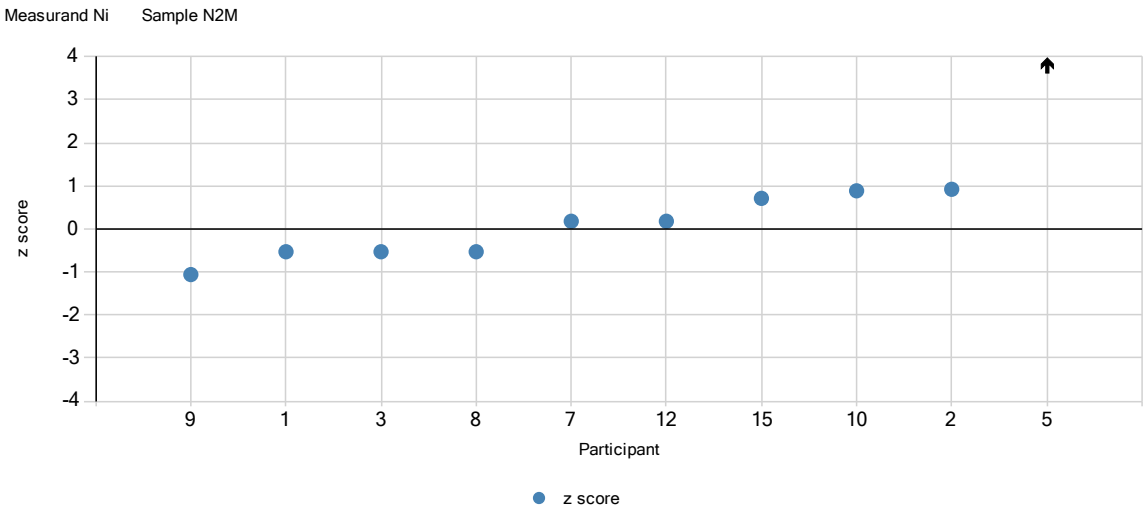
3
2
1
0
-1
-2
-3
-4
9 3 12 17 15 1 10 4 2 7 13 5
Participant
z score


Measurand Ni Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
5 9 4 3 12 7 17 10 2 1 8 15
Participant
z score


Measurand Ni Sample N2M
z score
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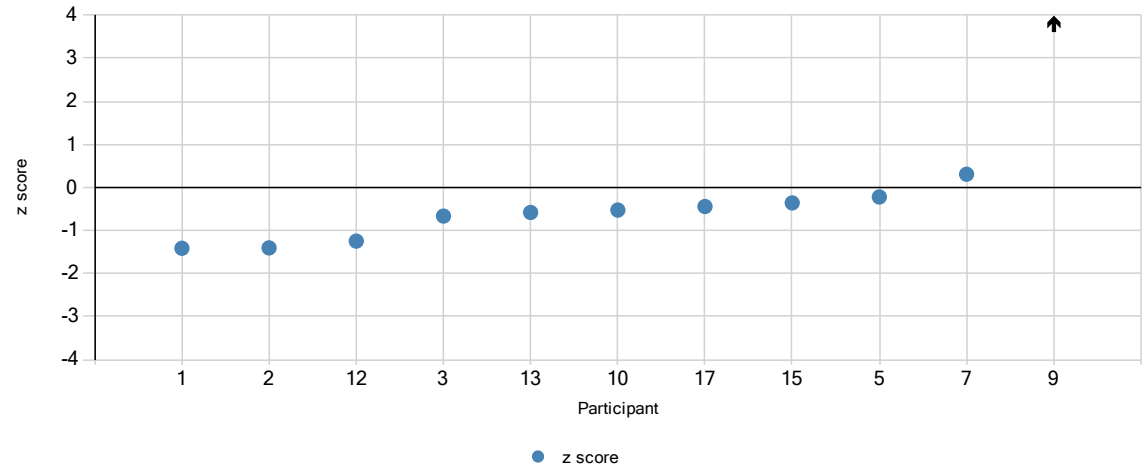
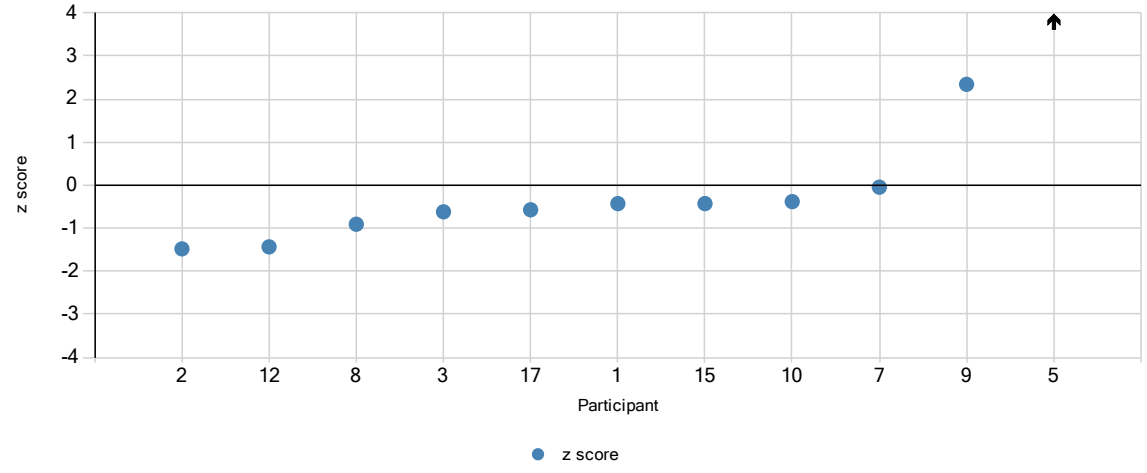
3
2
1
0
-1
-2
-3
-4
9 1 3 8 7 12 15 10 2 5
Participant
z score

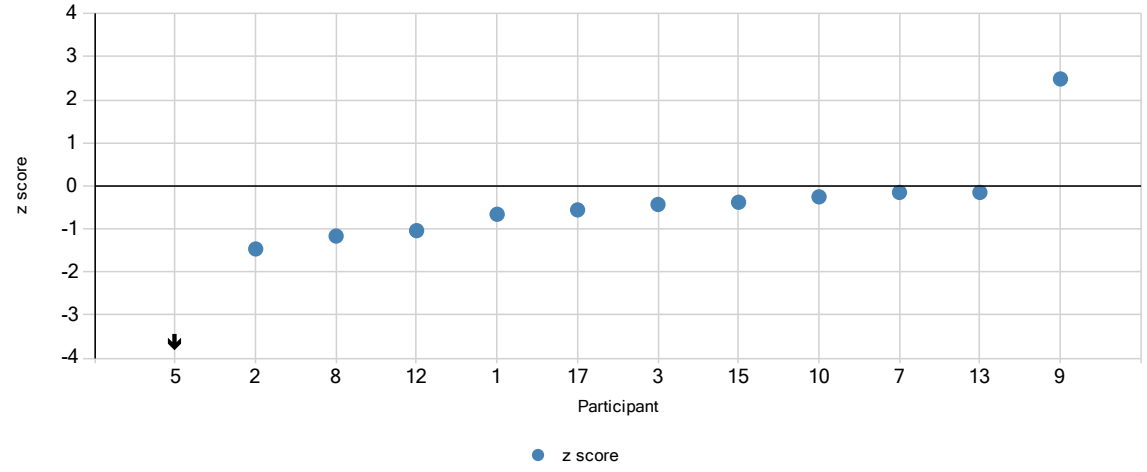
Measurand Pb Sample A1M

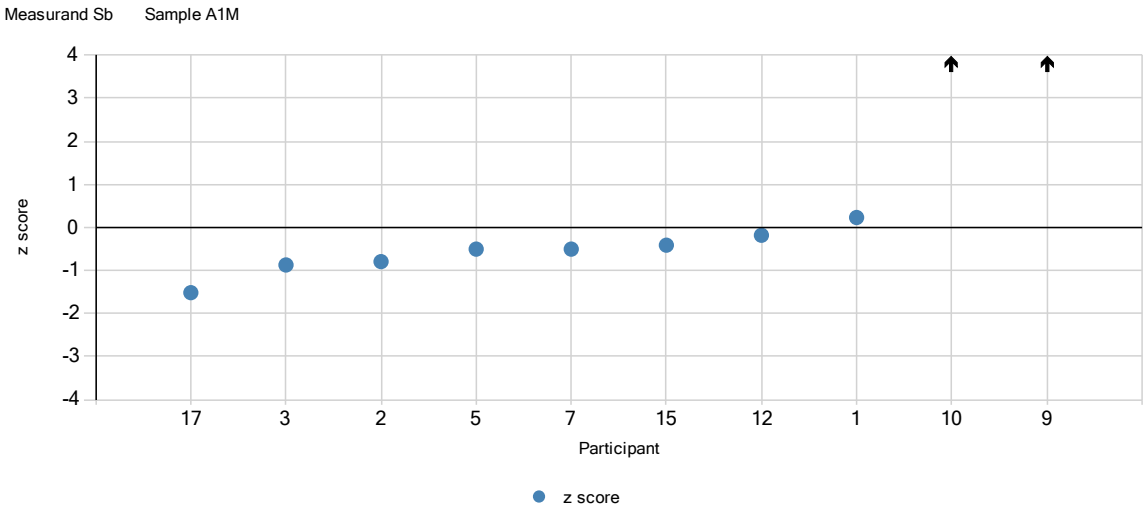


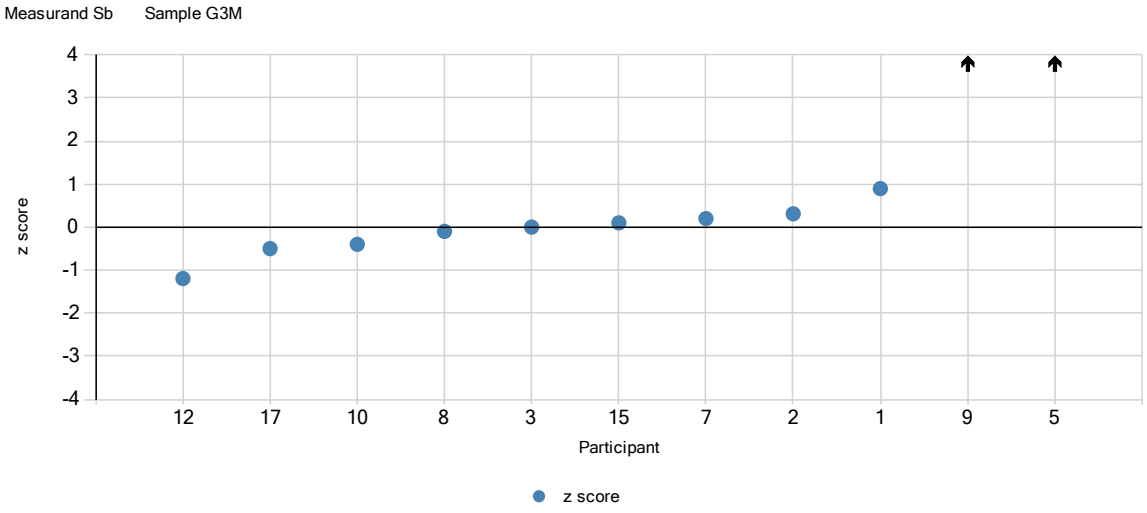

Measurand Pb Sample G3M

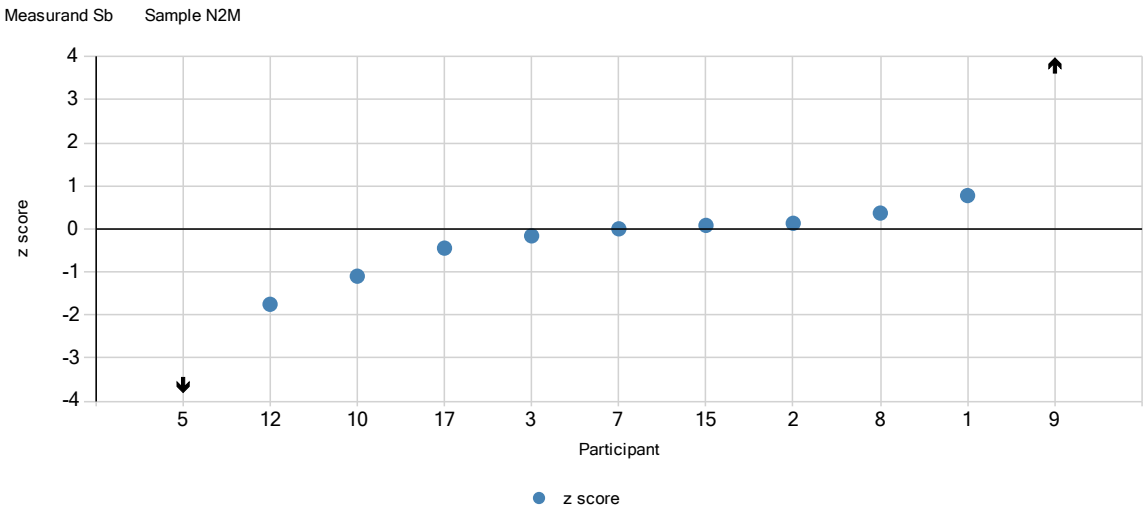



Measurand Pb Sample N2M

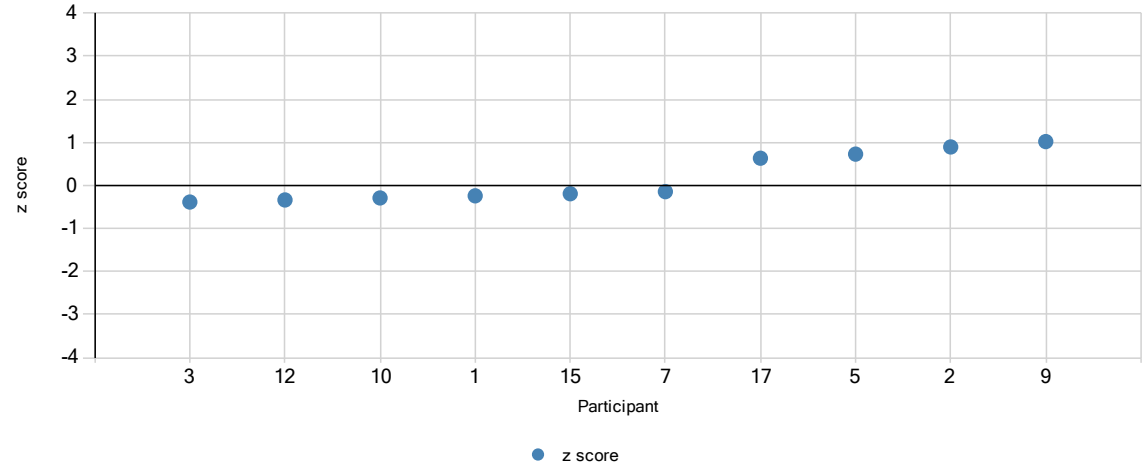



Measurand Sb Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
17 3 2 5 7 15 12 1 10 9
Participant
z score

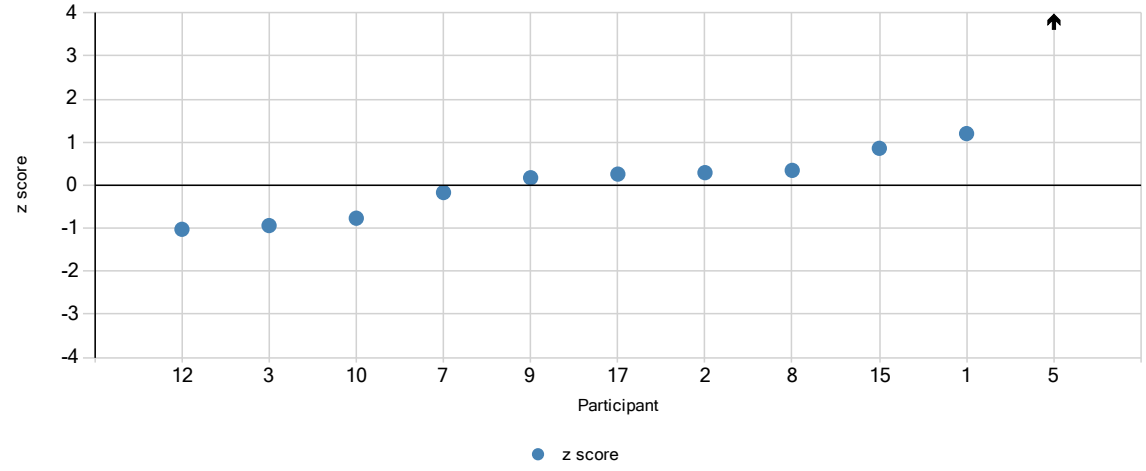

Measurand Sb Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
12 17 10 8 3 15 7 2 1 9 5
Participant
z score


Measurand Sb Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 12 10 17 3 7 15 2 8 1 9
Participant
z score

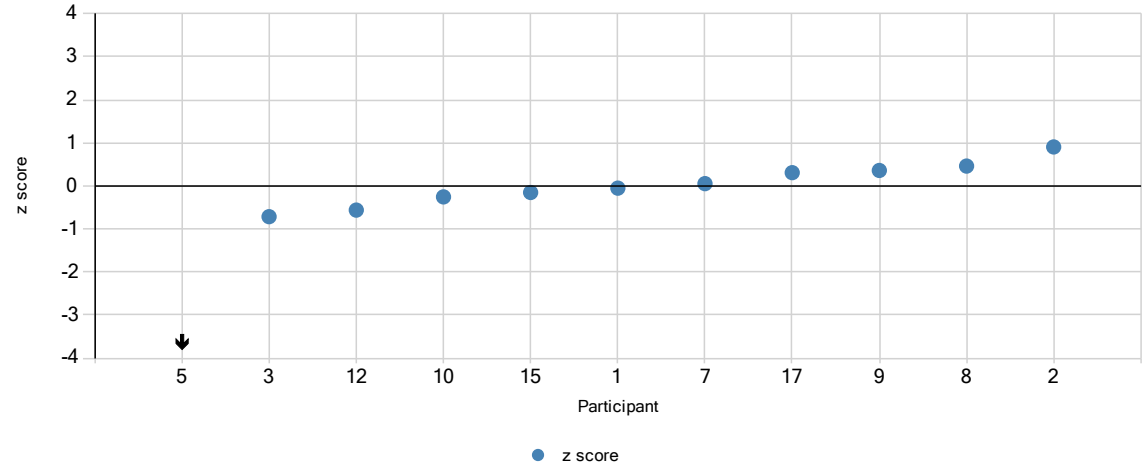
Measurand Se Sample A1M

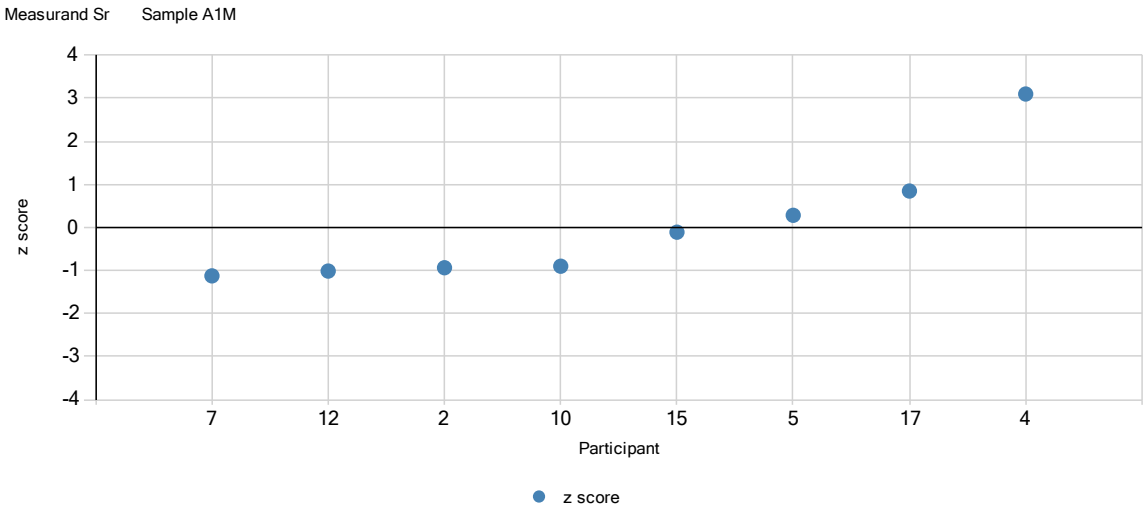


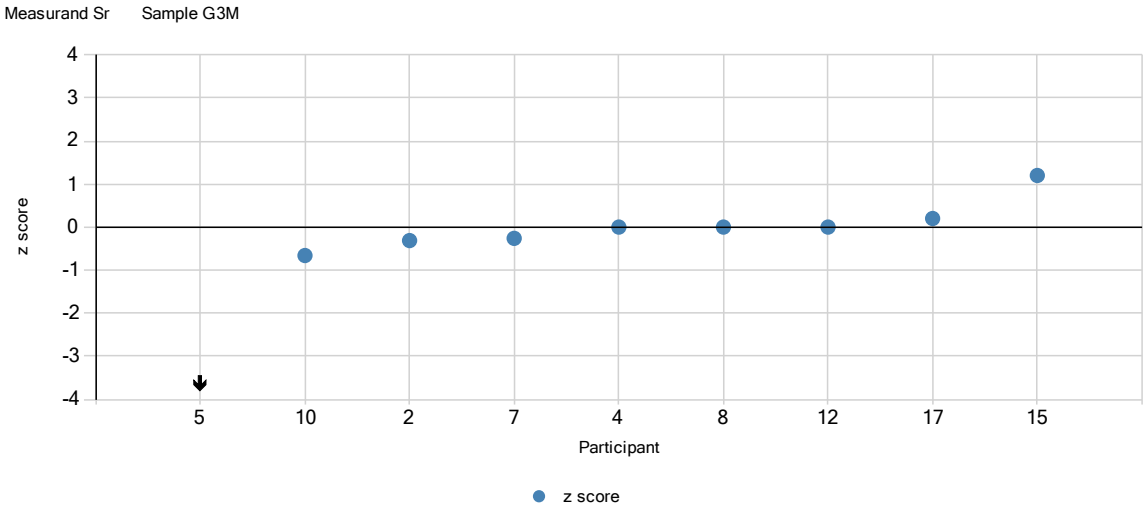

Measurand Se Sample G3M

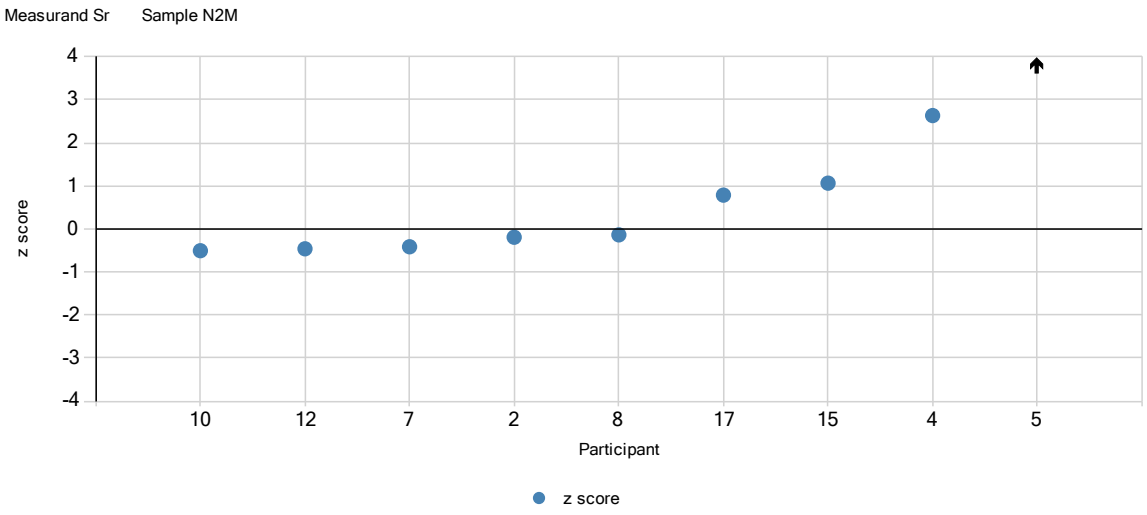



Measurand Se Sample N2M

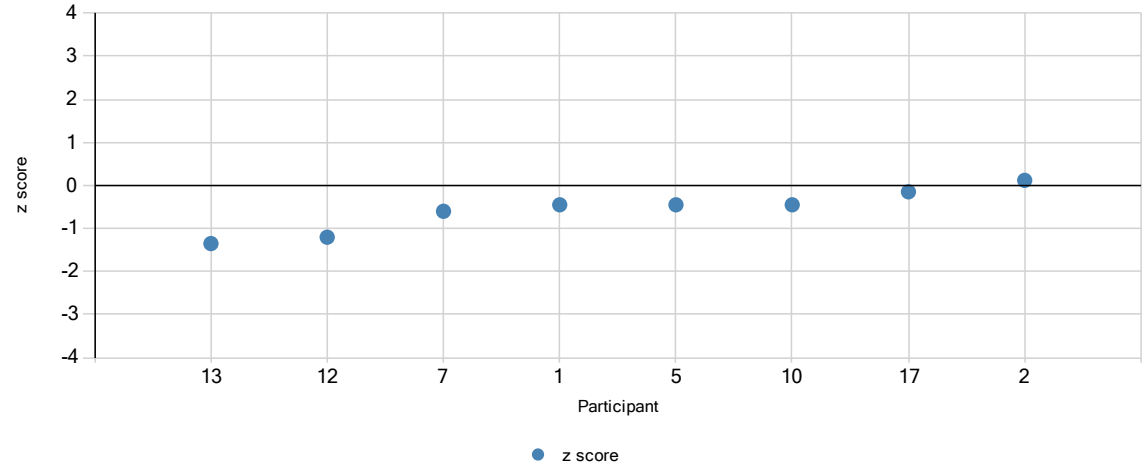



Measurand Sr
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
7
12
2
10
15
5
17
4
Participant
z score

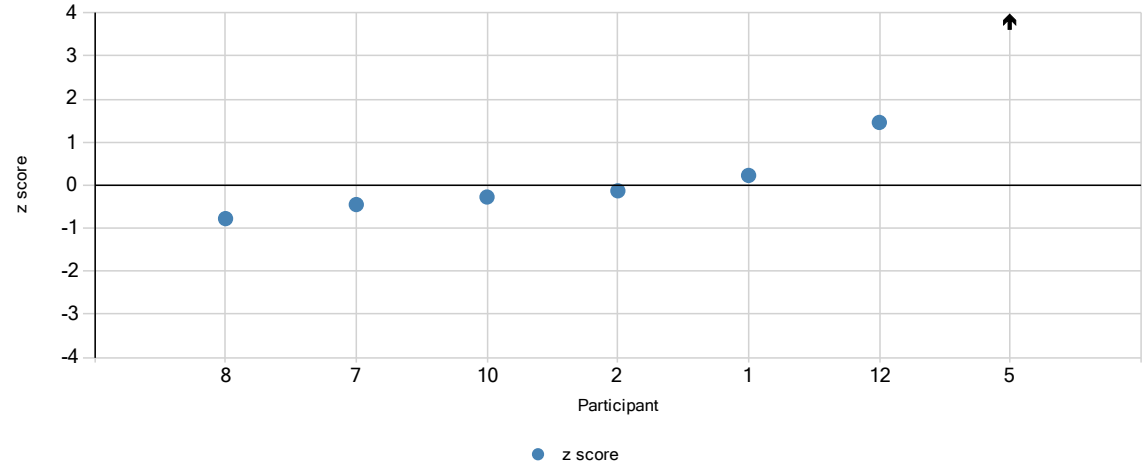

Measurand Sr
Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
5
10
2
7
4
8
12
17
15
Participant
z score


Measurand Sr
Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
10
12
7
2
8
17
15
4
5
Participant
z score

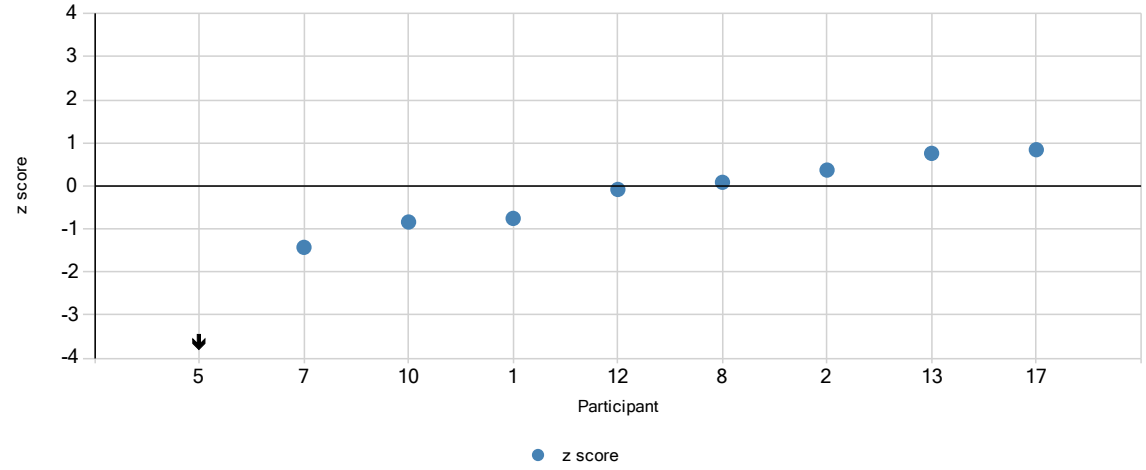
Measurand Ti Sample A1M

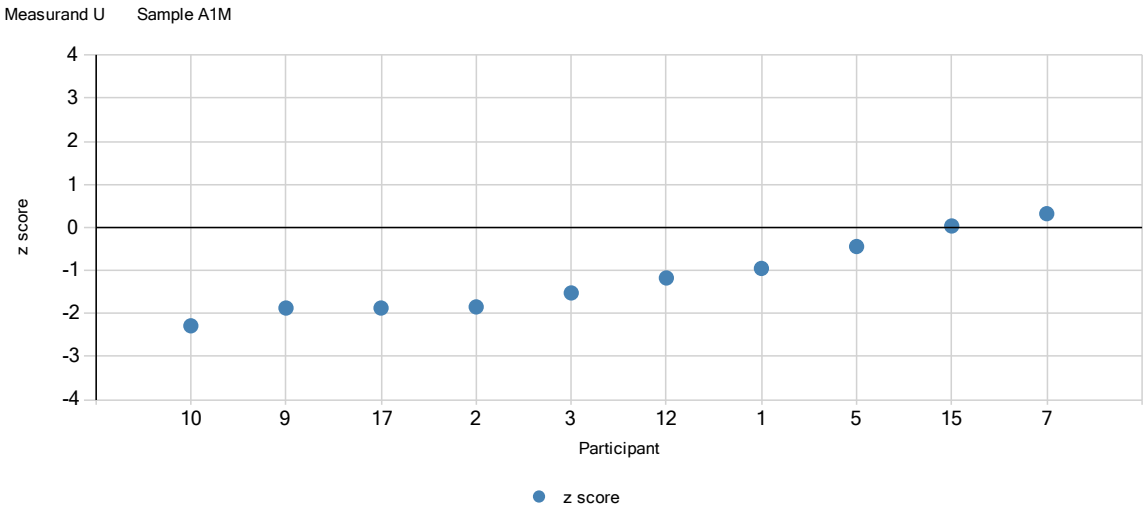


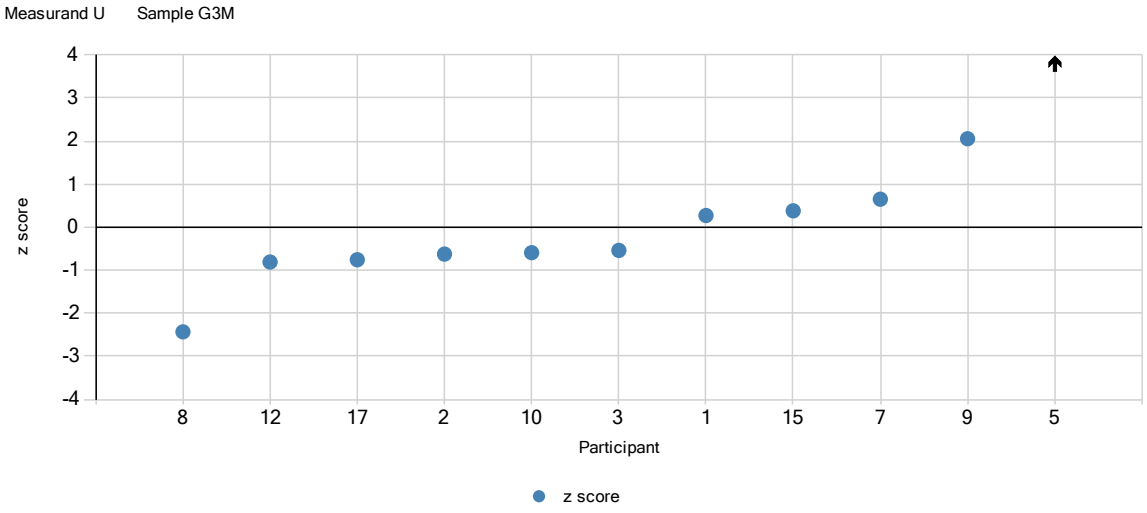

Measurand Ti Sample G3M

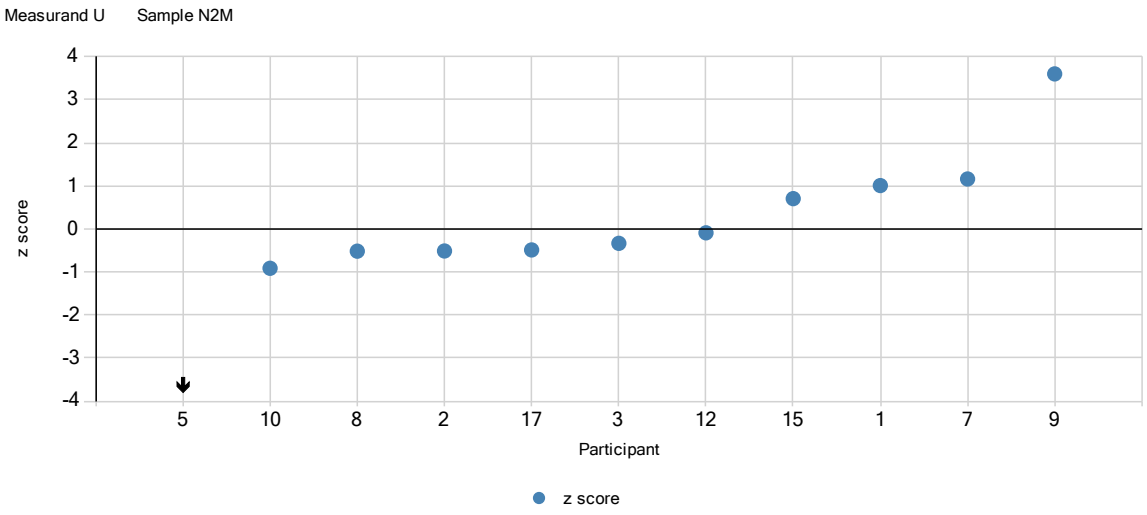



Measurand Ti Sample N2M

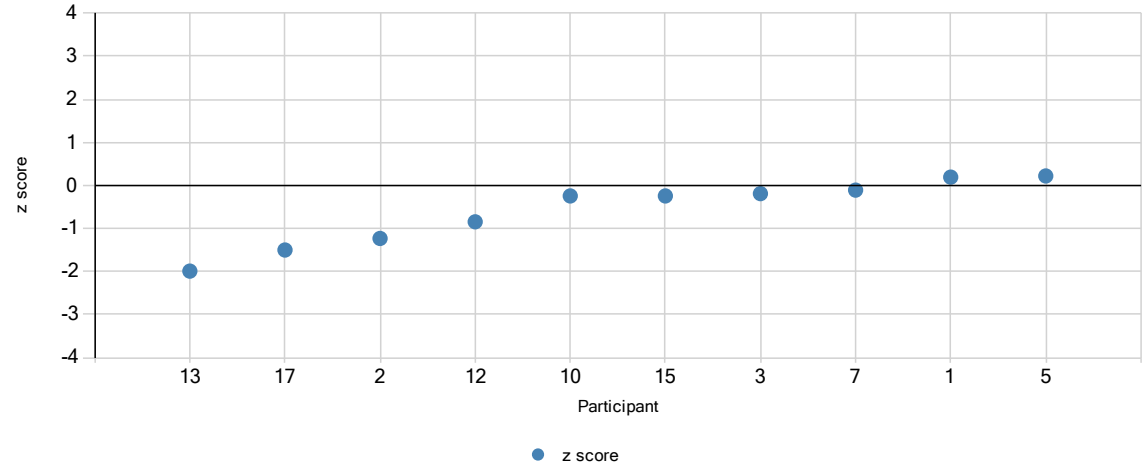



Measurand U
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
10
9
17
2
3
12
1
5
15
7
Participant
z score

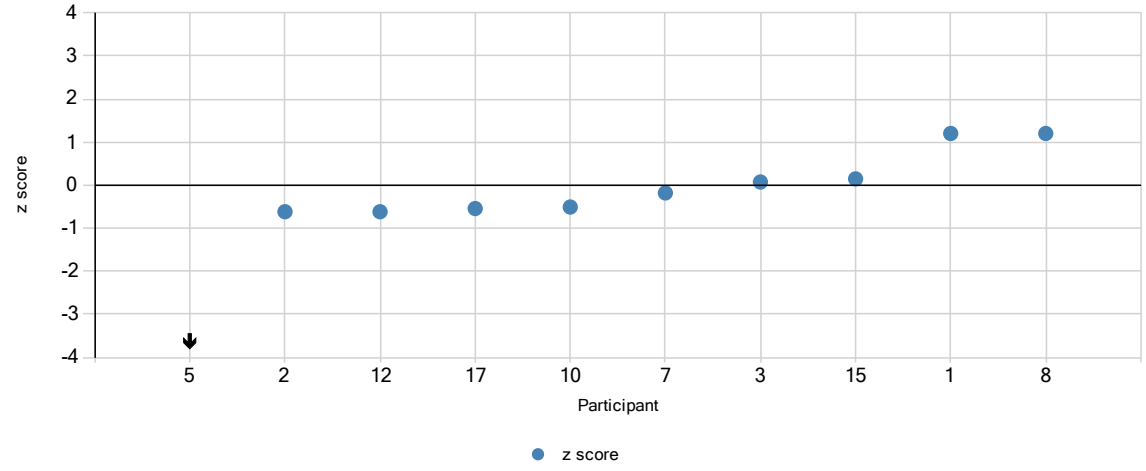

Measurand U
Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
8
12
17
2
10
3
1
15
7
9
5
Participant
z score


Measurand U
Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
5
10
8
2
17
3
12
15
1
7
9
Participant
z score

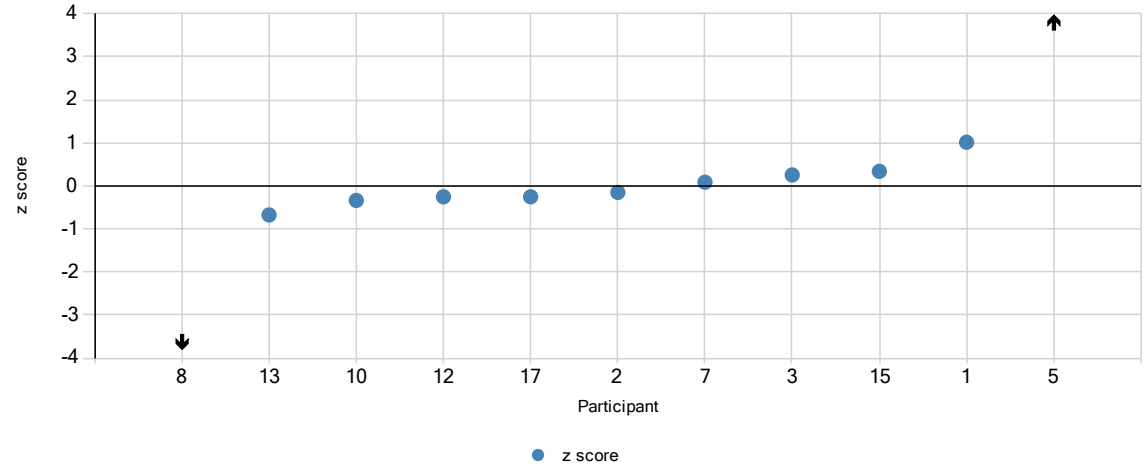
Measurand V Sample A1M

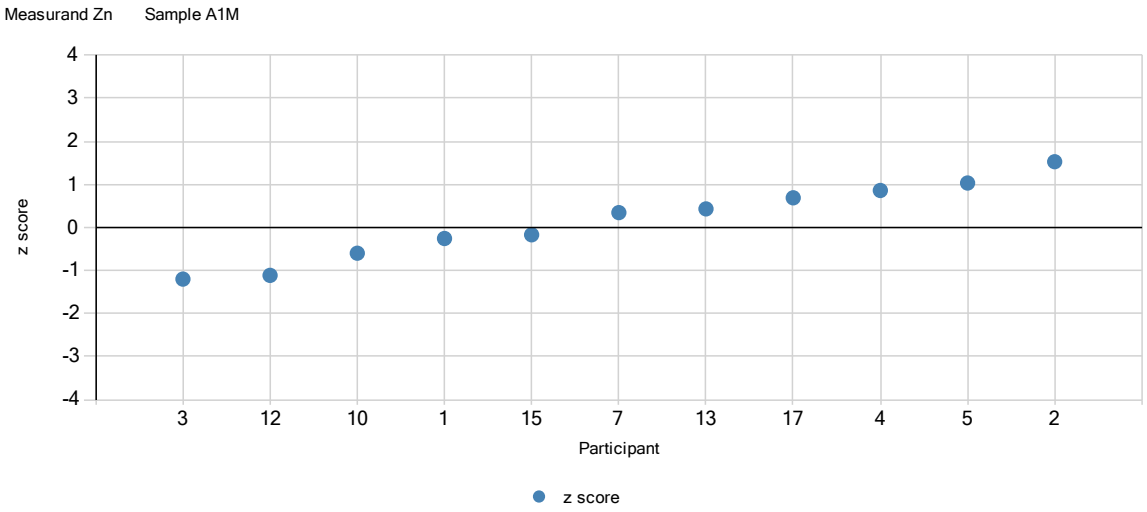


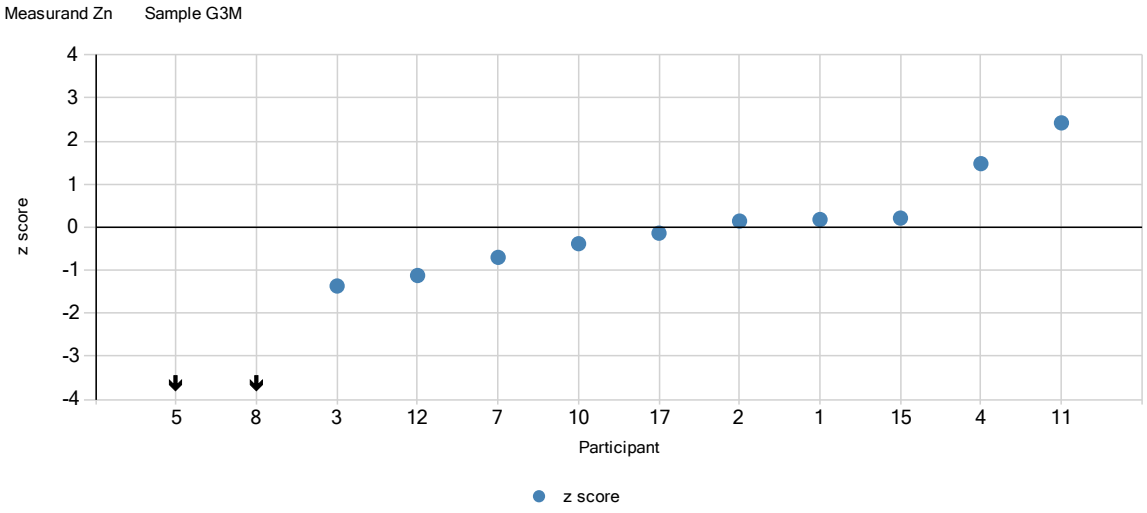

Measurand V Sample G3M

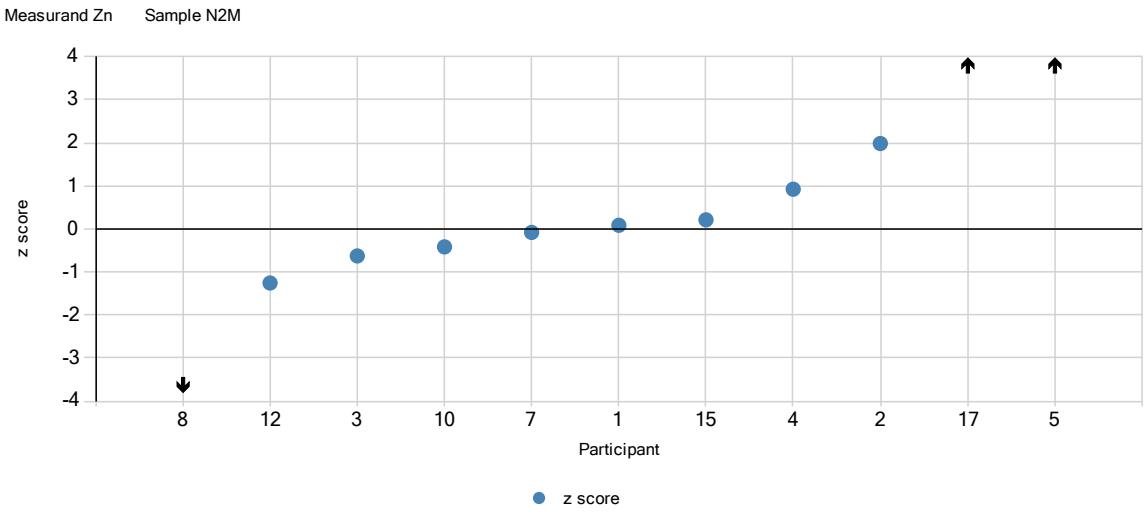



Measurand V Sample N2M




Measurand Zn Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
3 12 10 1 15 7 13 17 4 5 2
Participant
z score

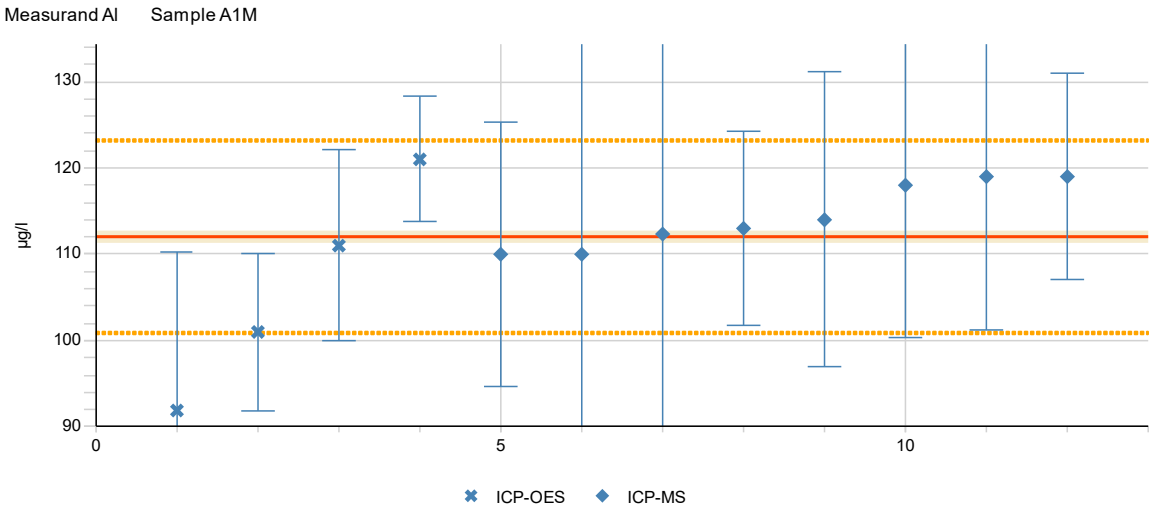

Measurand Zn Sample G3M
z score
4
3
2
1
0
-1
-2
-3
-4
5 8 3 12 7 10 17 2 1 15 4 11
Participant
z score

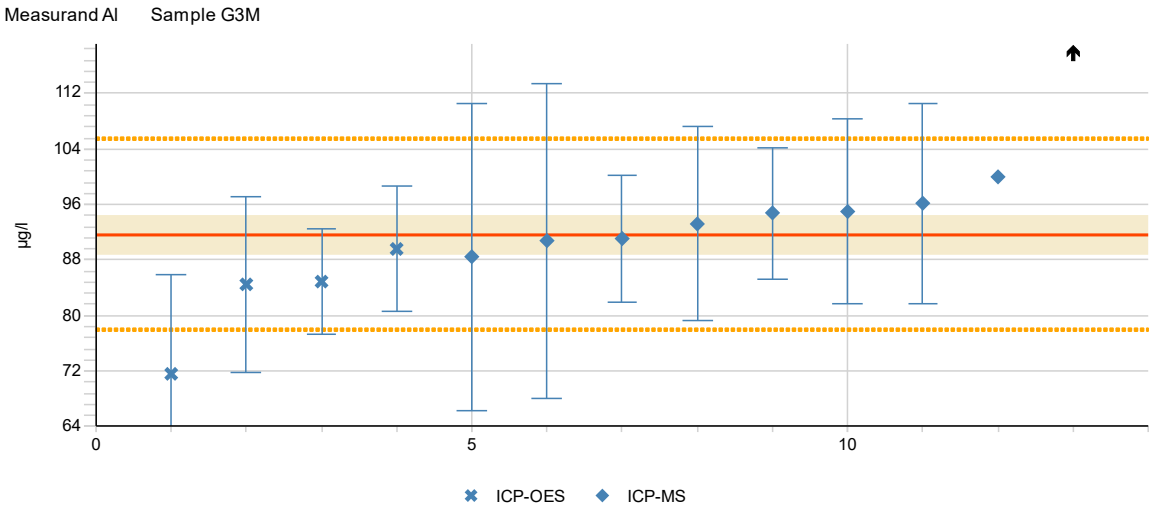

Measurand Zn Sample N2M
z score
4
3
2
1
0
-1
-2
-3
-4
8 12 3 10 7 1 15 4 2 17 5
Participant
z score

# APPENDIX 10: Results grouped according to the methods

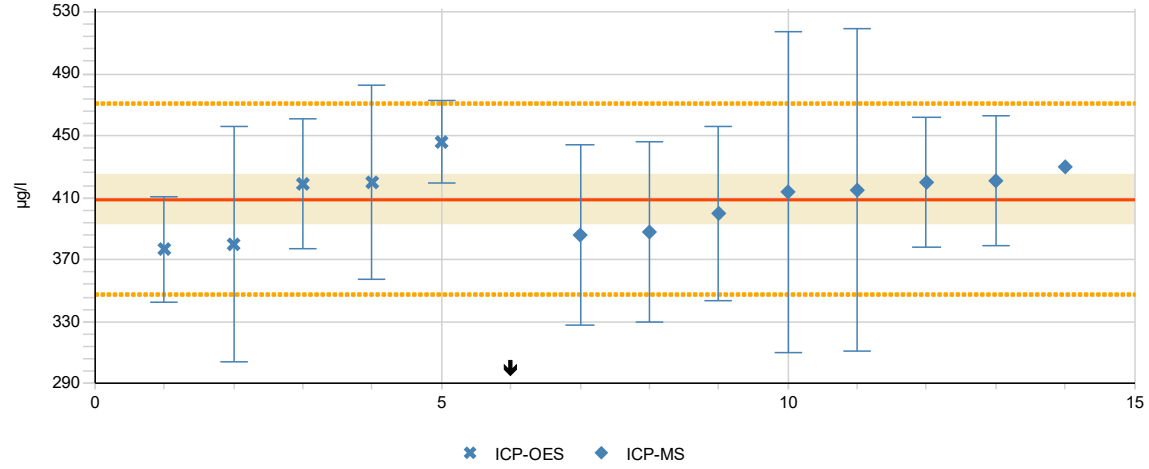
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

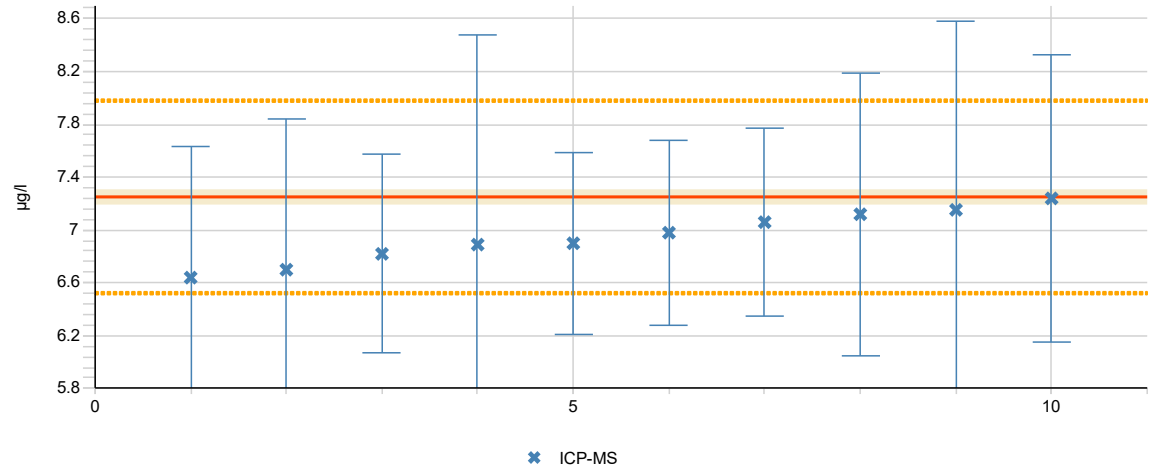


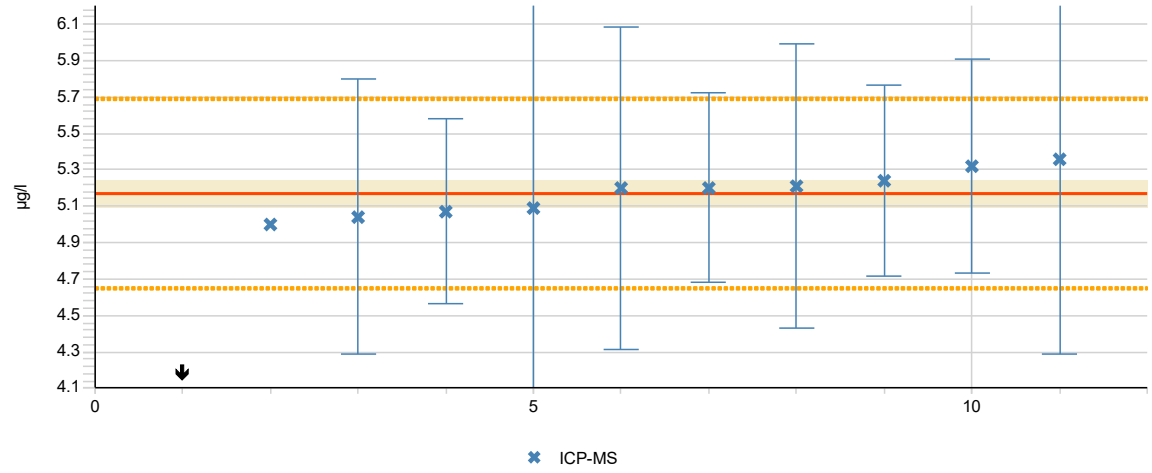
Measurand Al Sample N2M



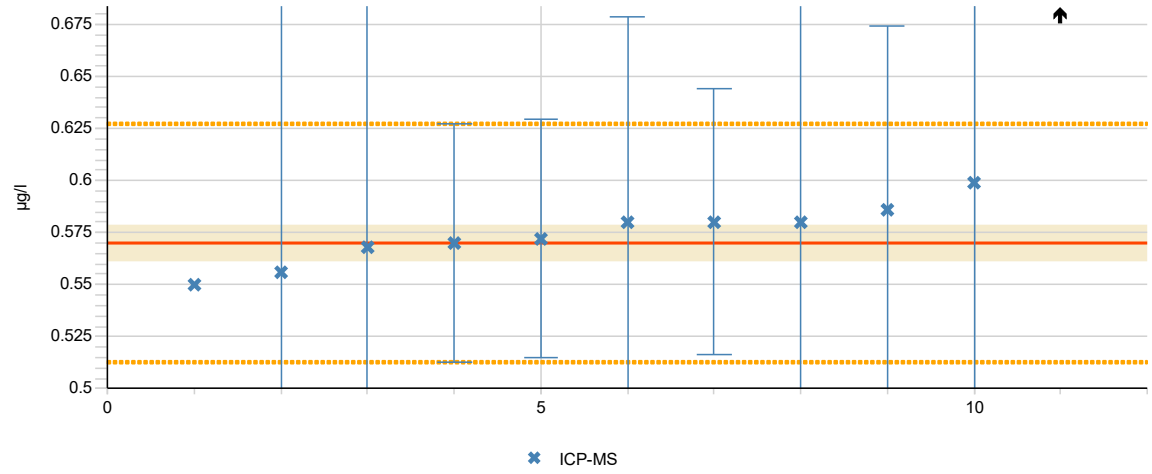

Measurand As Sample A1M



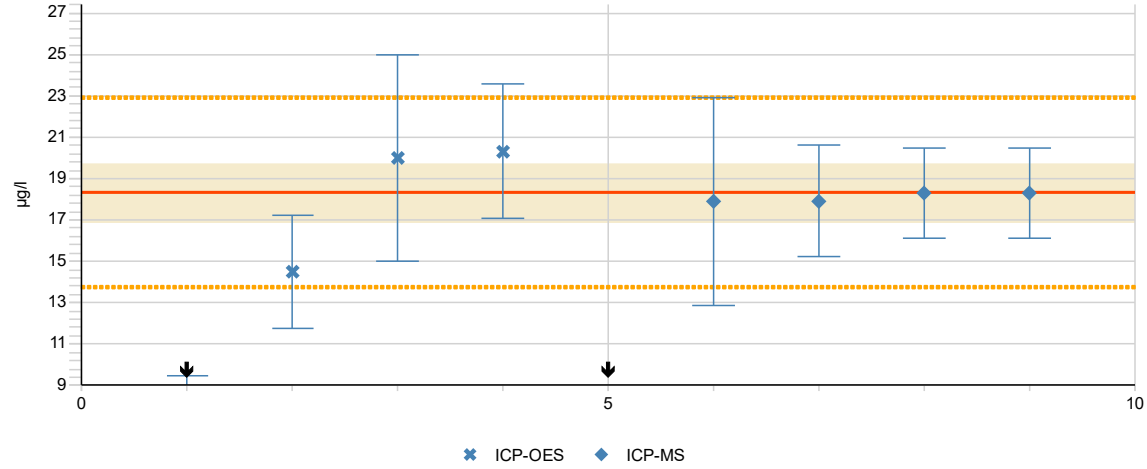

Measurand As Sample G3M



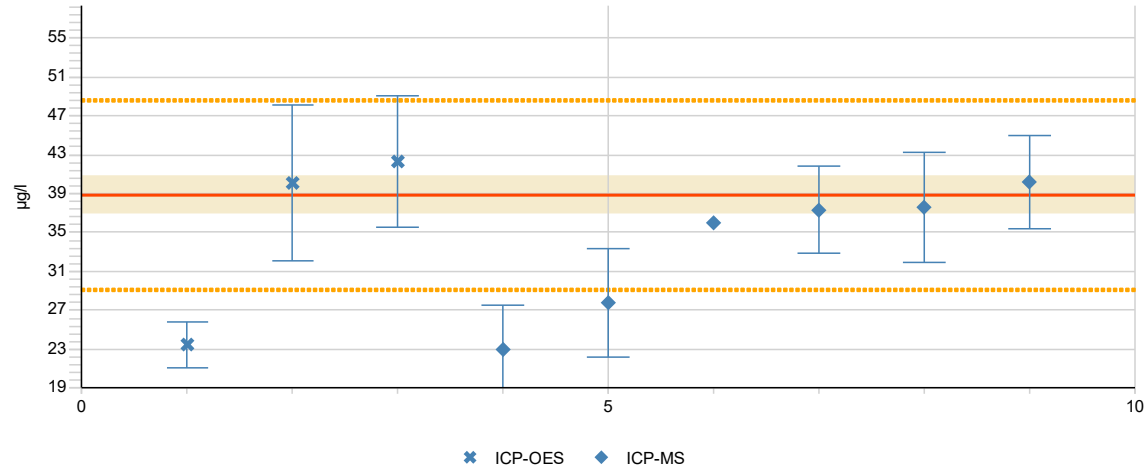
Measurand As Sample N2M



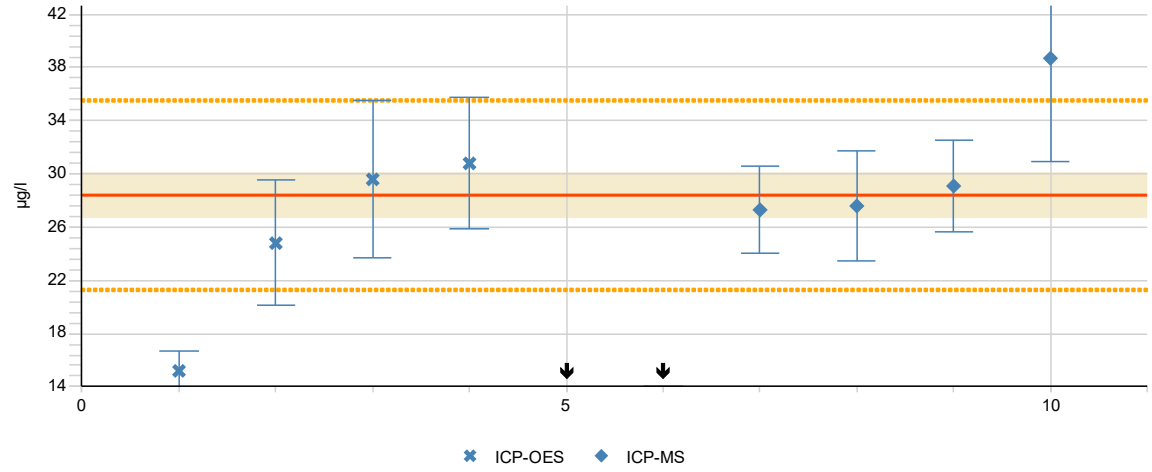

Measurand B Sample A1M



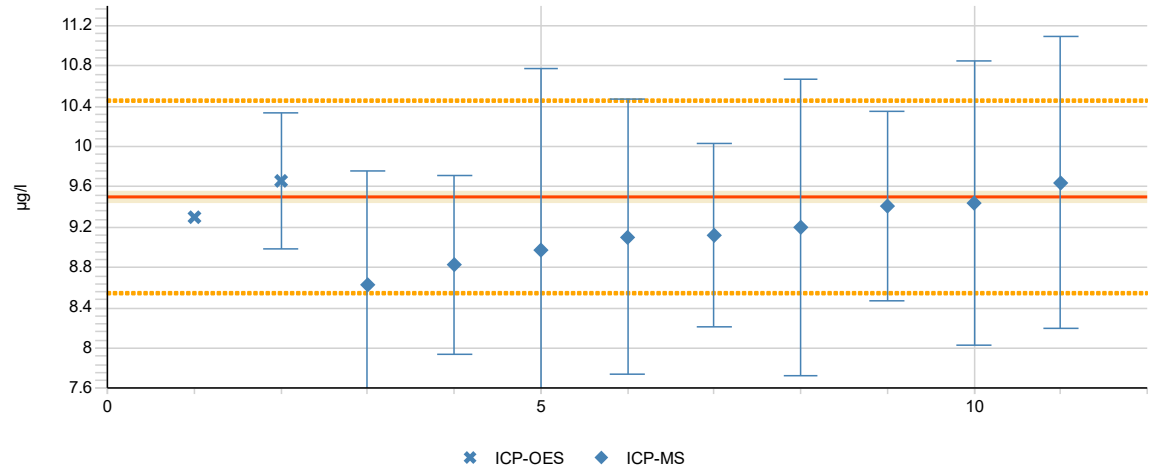

Measurand B Sample G3M



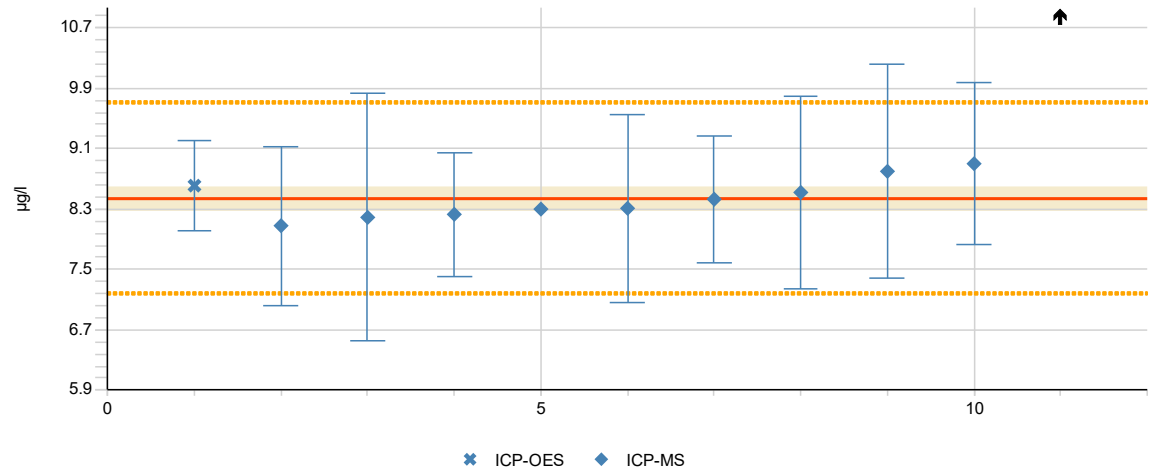
Measurand B Sample N2M



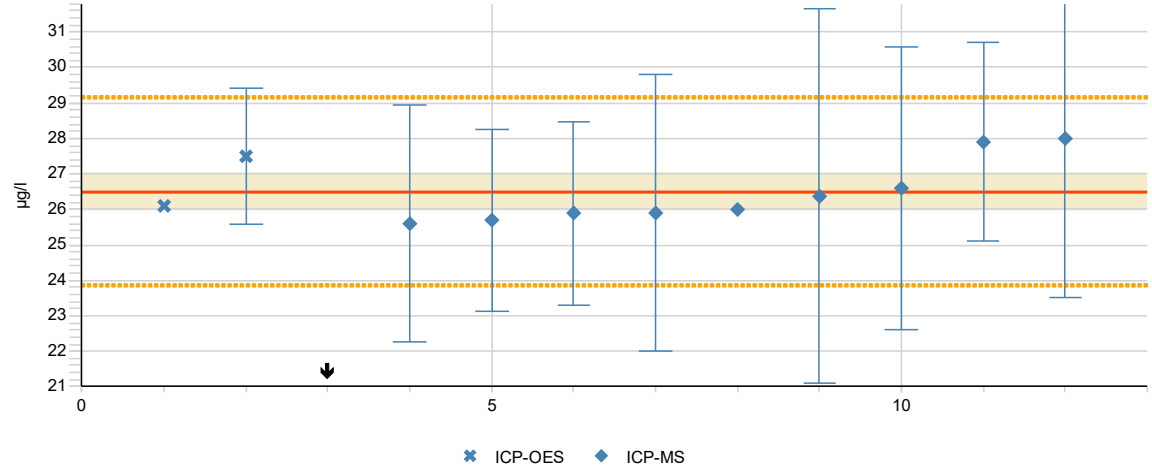

Measurand Ba Sample A1M



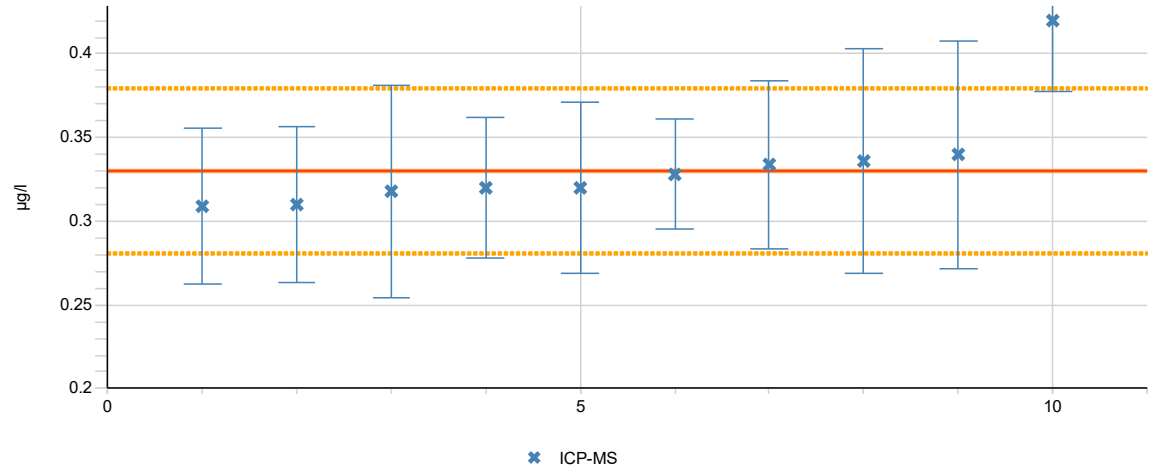

Measurand Ba Sample G3M



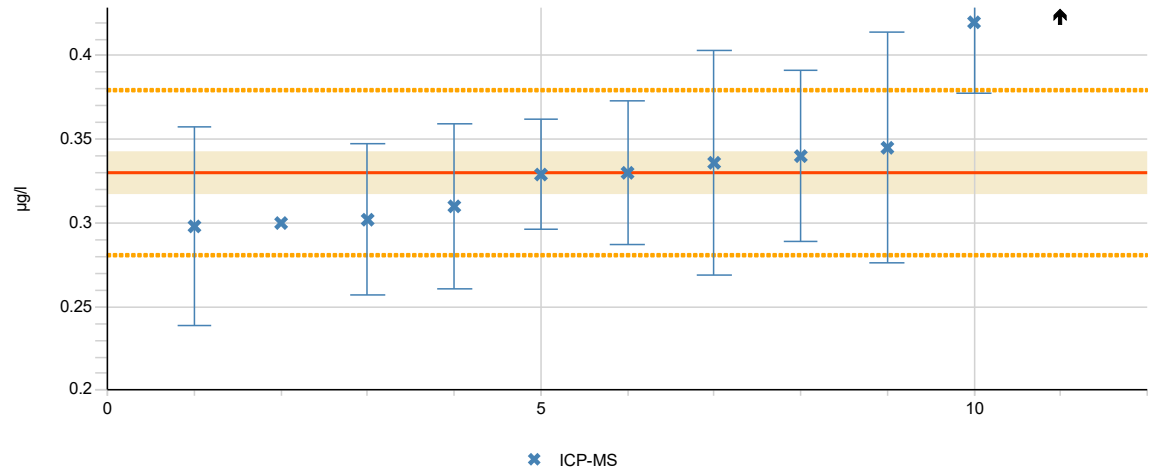
Measurand Ba Sample N2M

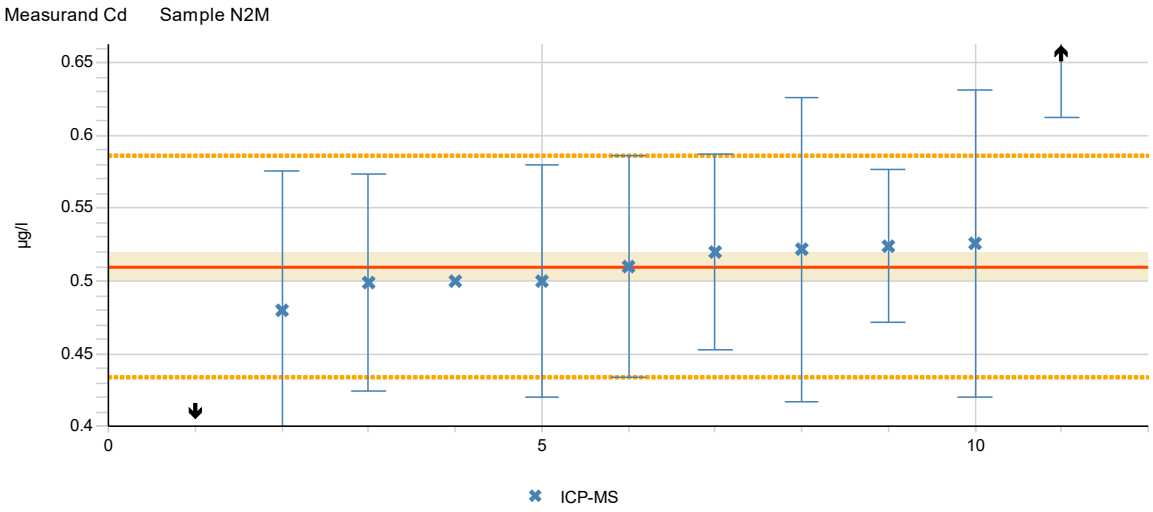


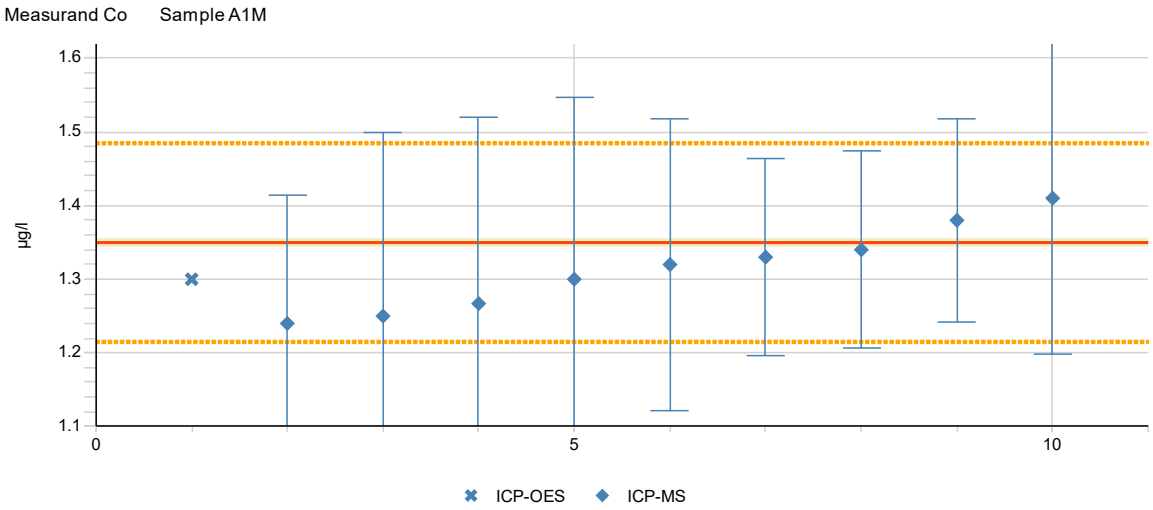

Measurand Cd Sample A1M

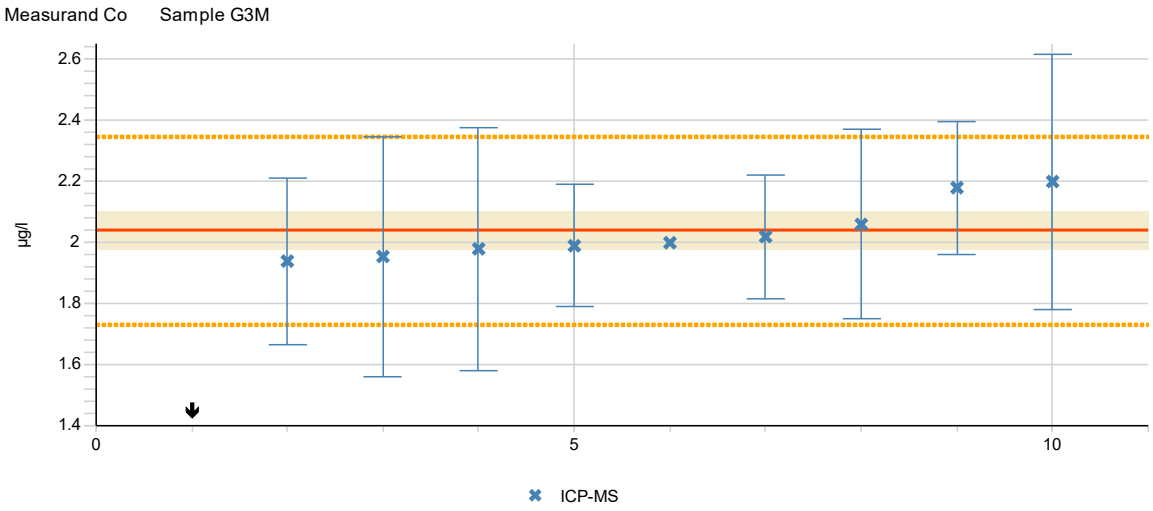



Measurand Cd Sample G3M

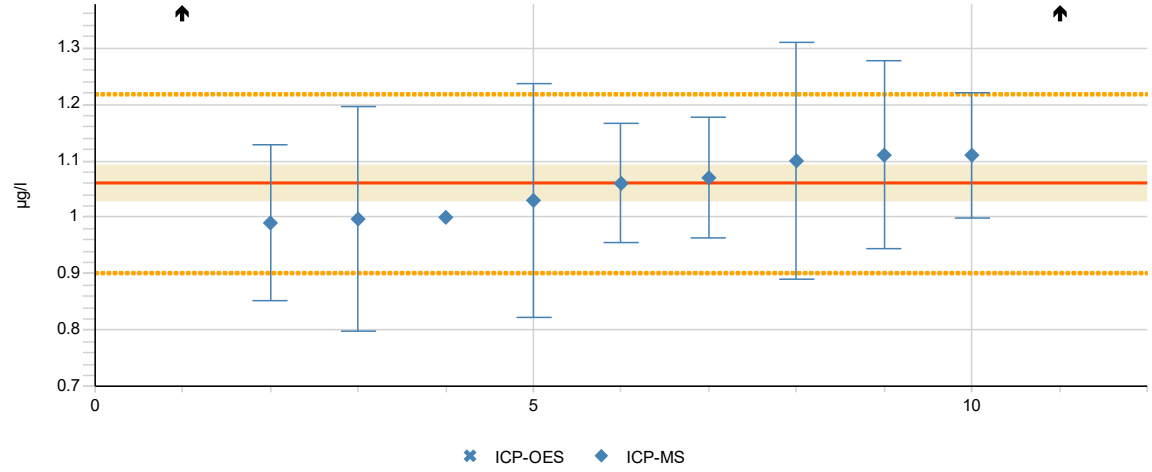



Measurand Cd
Sample N2M
µg/l
0.65
0.6
0.55
0.5
0.45
0.4
0
5
10
ICP-MS

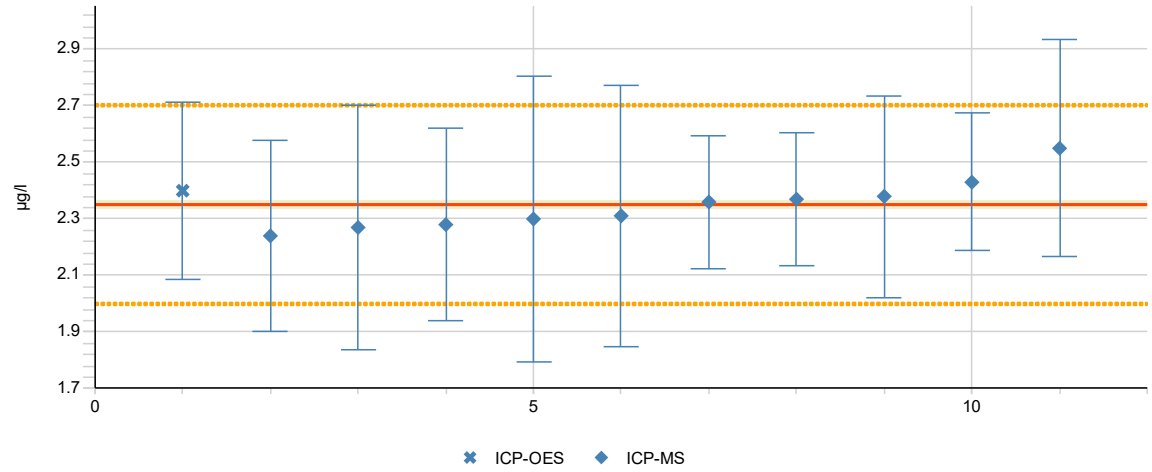

Measurand Co
Sample A1M
µg/l
1.6
1.5
1.4
1.3
1.2
1.1
0
5
10
ICP-OES
ICP-MS


Measurand Co
Sample G3M
µg/l
2.6
2.4
2.2
2
1.8
1.6
1.4
0
5
10
ICP-MS

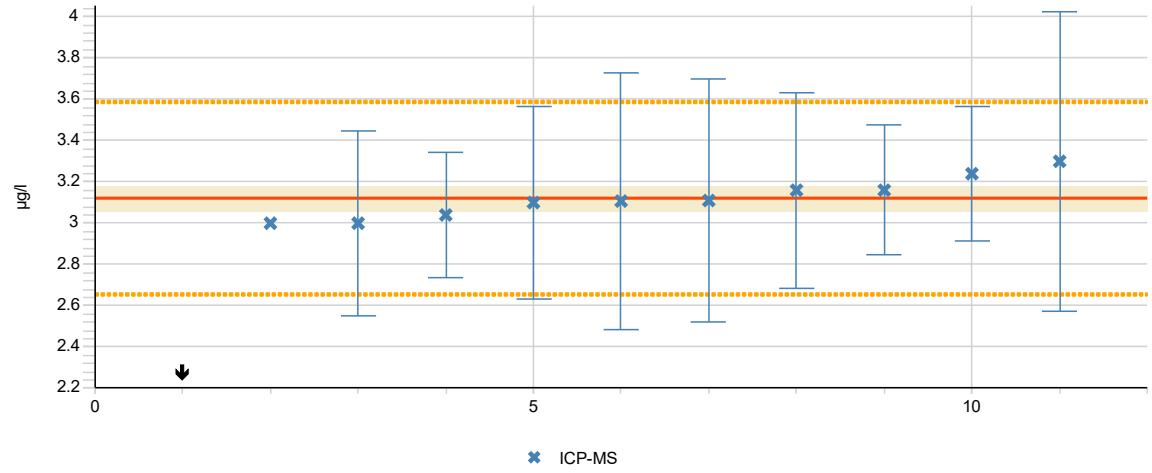
Measurand Co Sample N2M



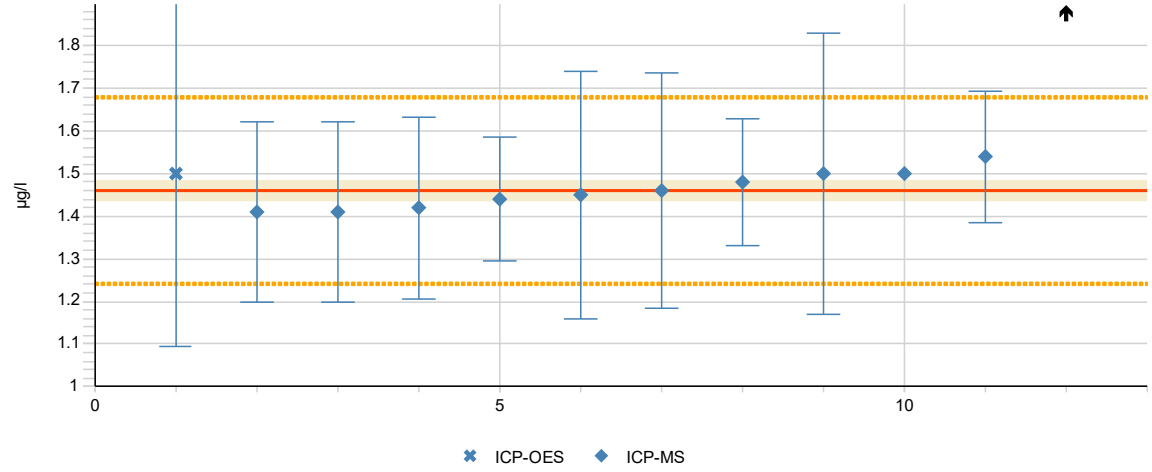

Measurand Cr Sample A1M



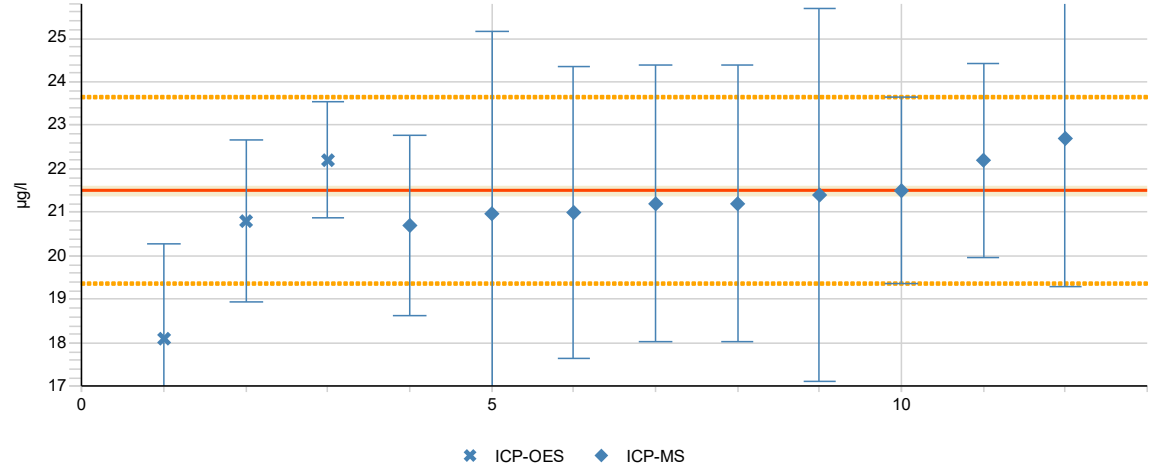

Measurand Cr Sample G3M



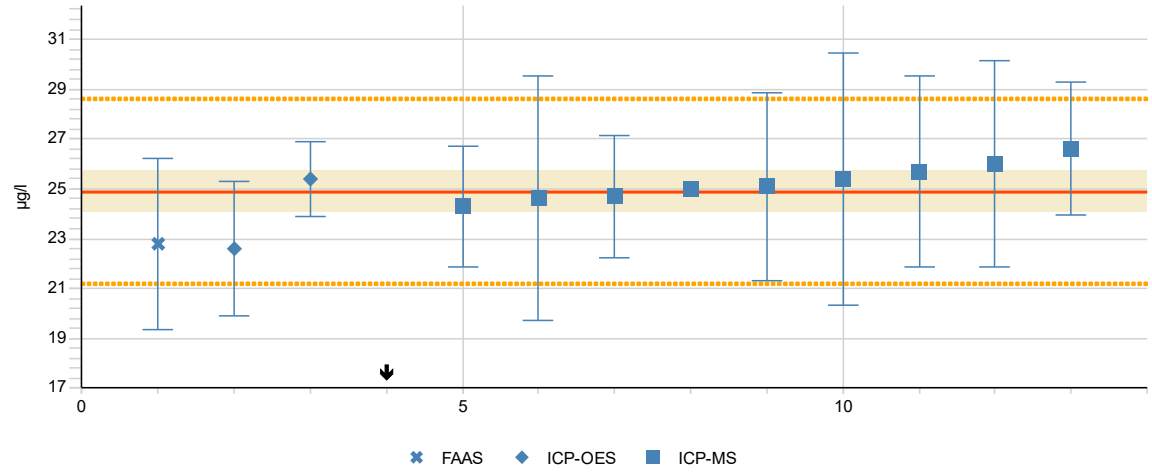
Measurand Cr Sample N2M



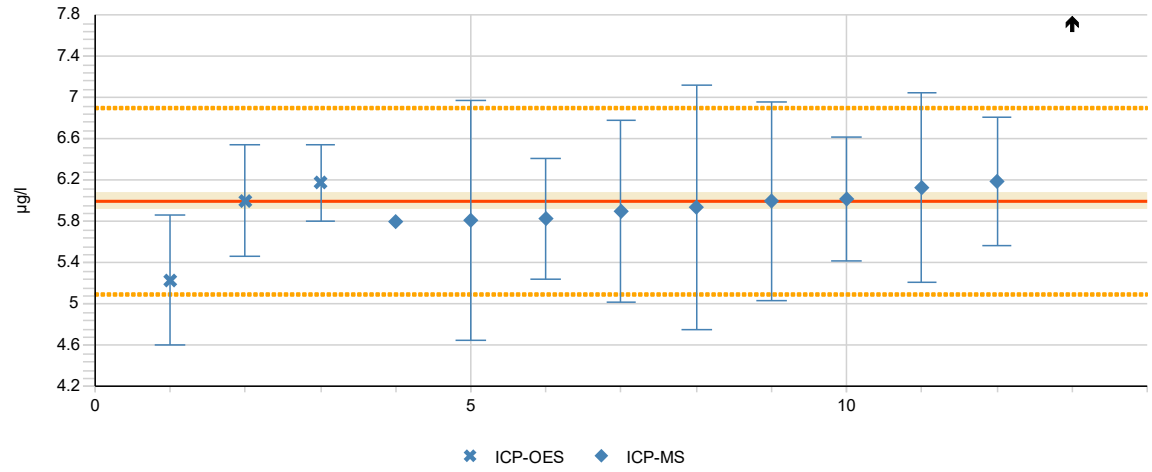

Measurand Cu Sample A1M



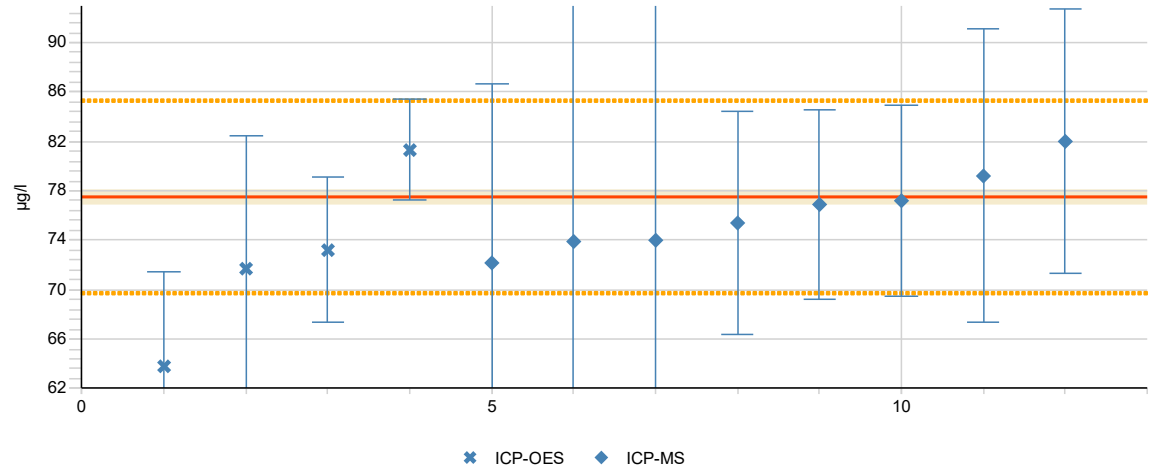

Measurand Cu Sample G3M



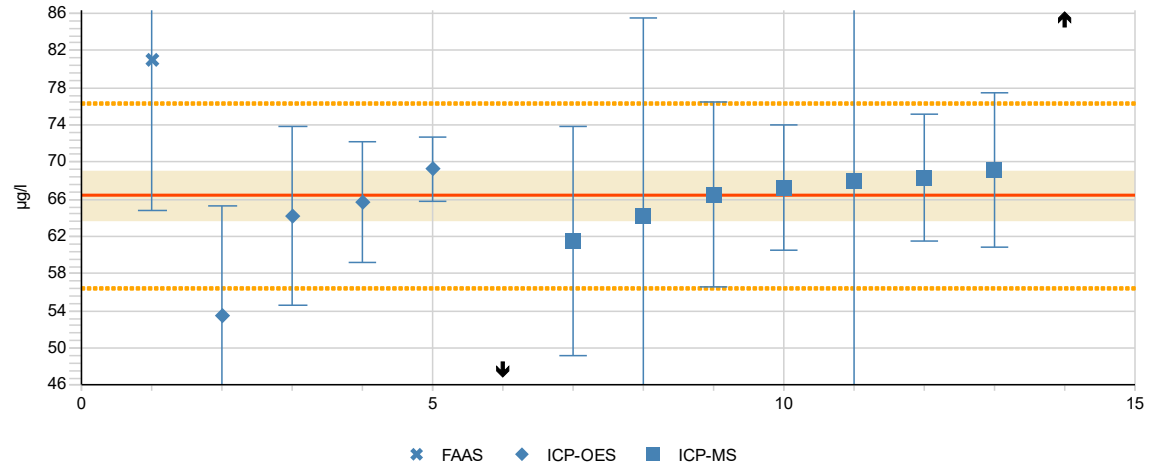
Measurand Cu Sample N2M

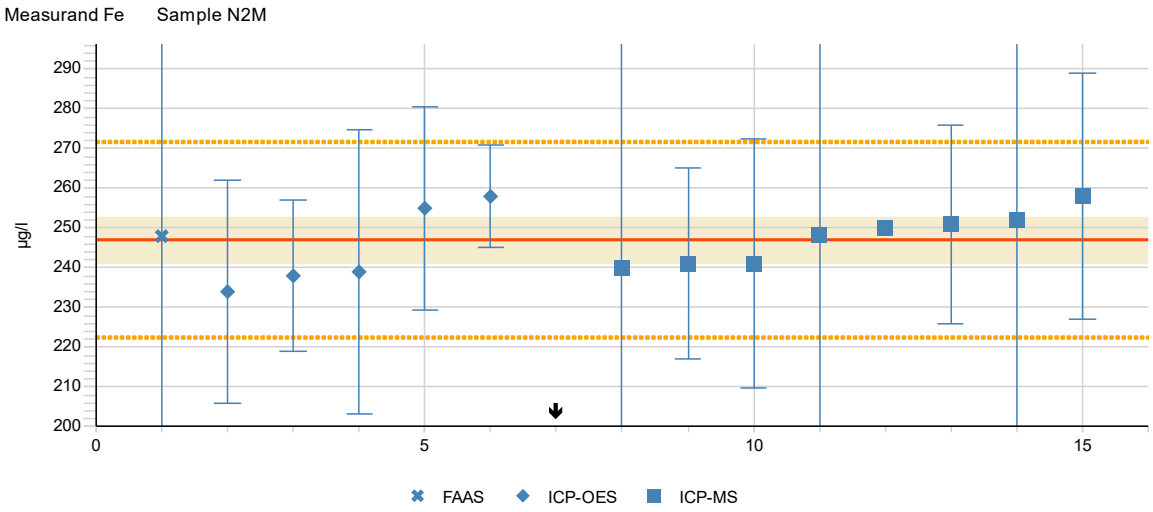


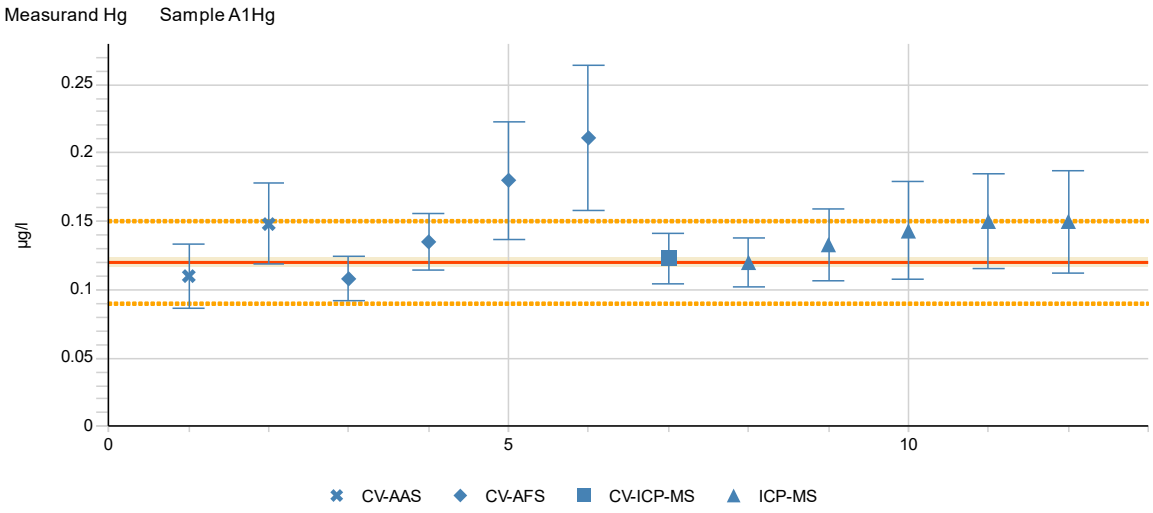

Measurand Fe Sample A1M

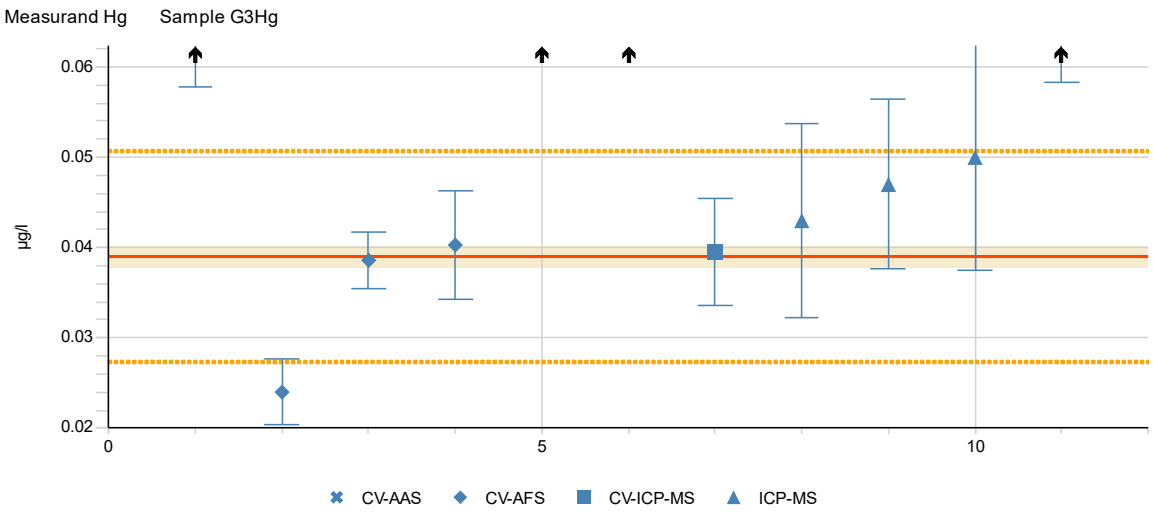



Measurand Fe Sample G3M

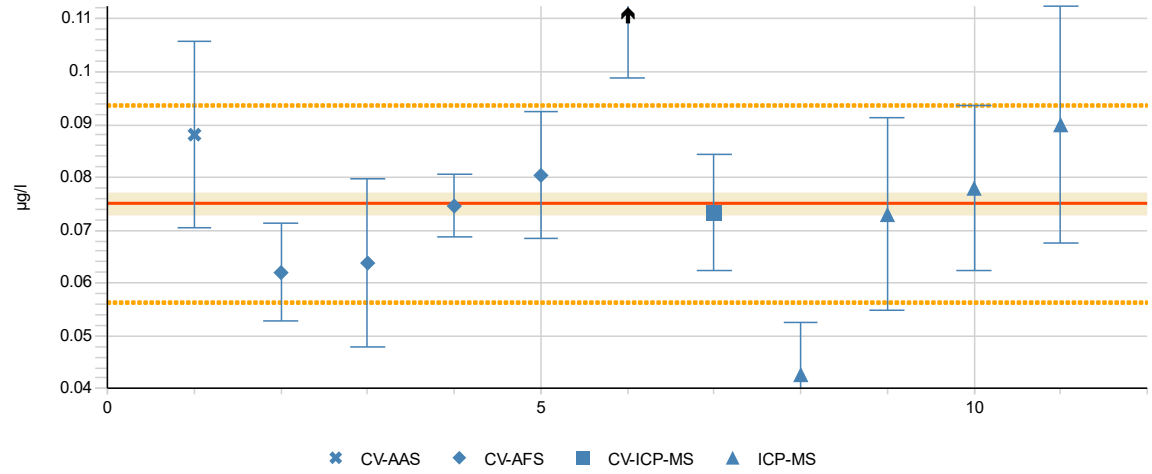



Measurand Fe Sample N2M
µg/l
290
280
270
260
250
240
230
220
210
200
0
5
10
15
FAAS
ICP-OES
ICP-MS

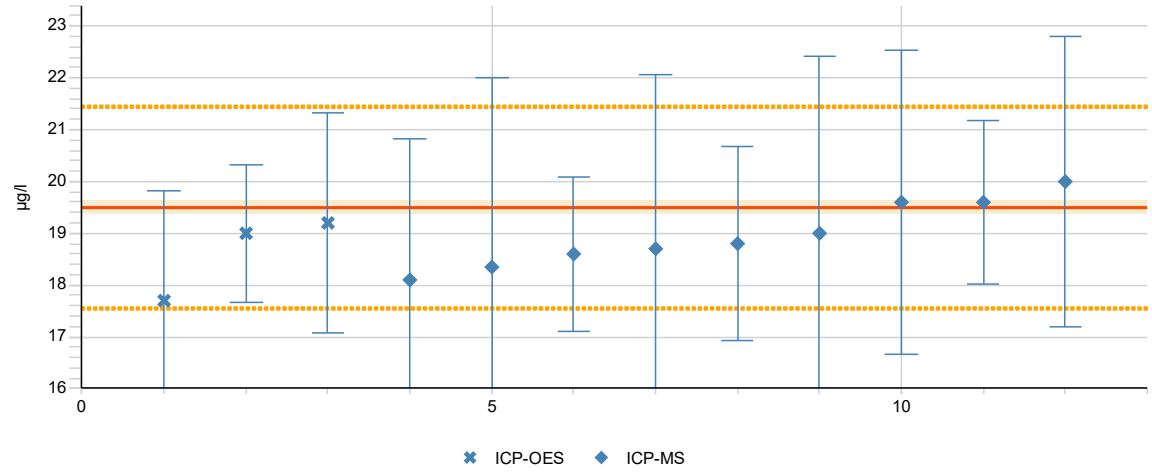

Measurand Hg Sample A1Hg
µg/l
0.25
0.2
0.15
0.1
0.05
0
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS


Measurand Hg Sample G3Hg
µg/l
0.06
0.05
0.04
0.03
0.02
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS

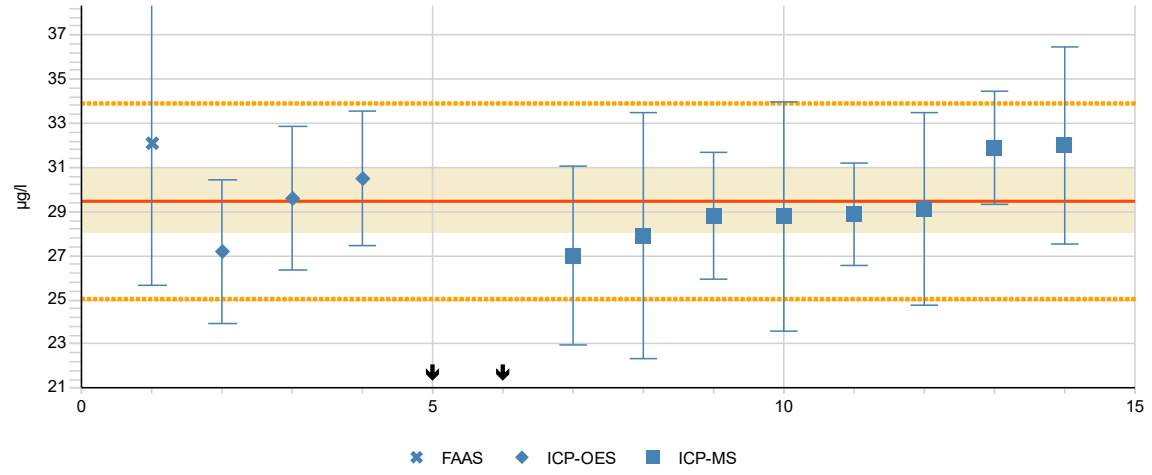
Measurand Hg Sample N2Hg



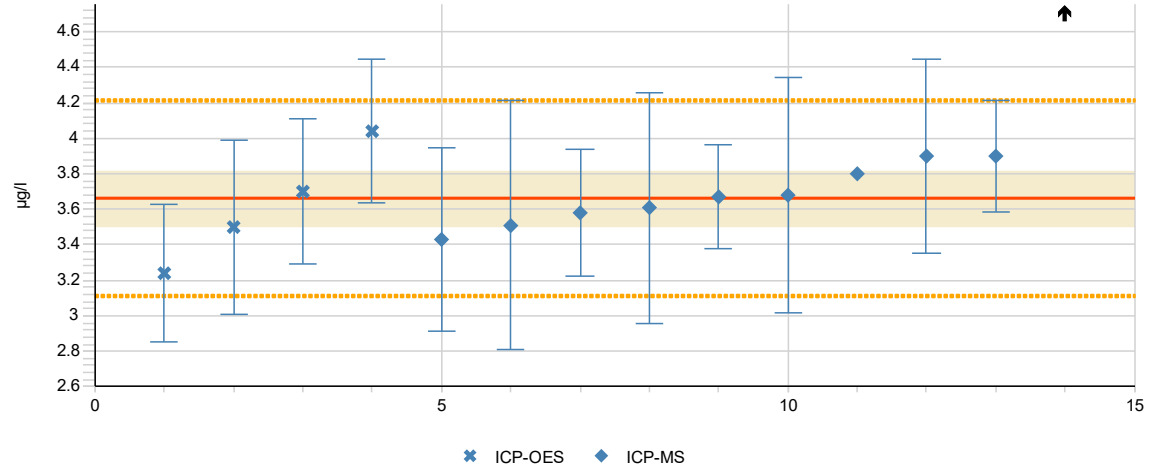

Measurand Mn Sample A1M



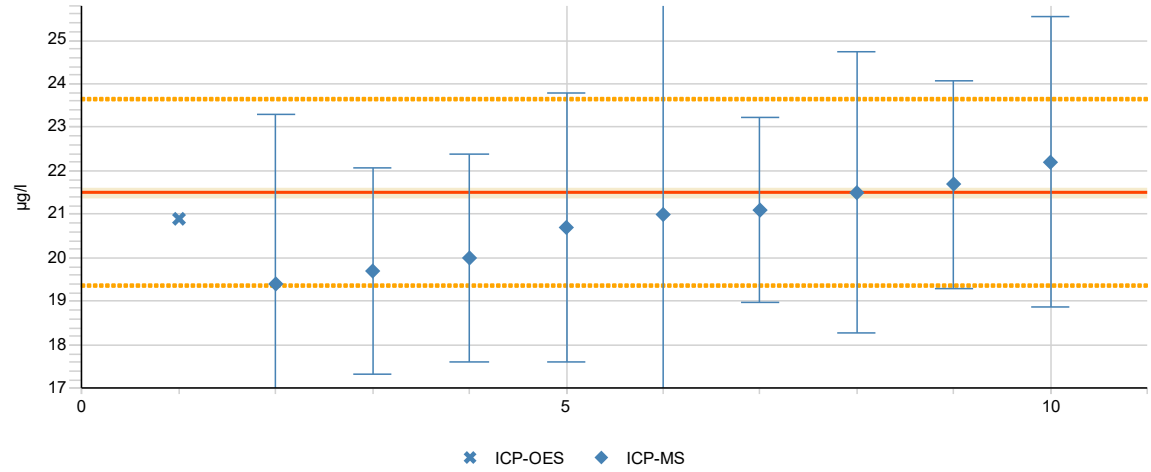

Measurand Mn Sample G3M



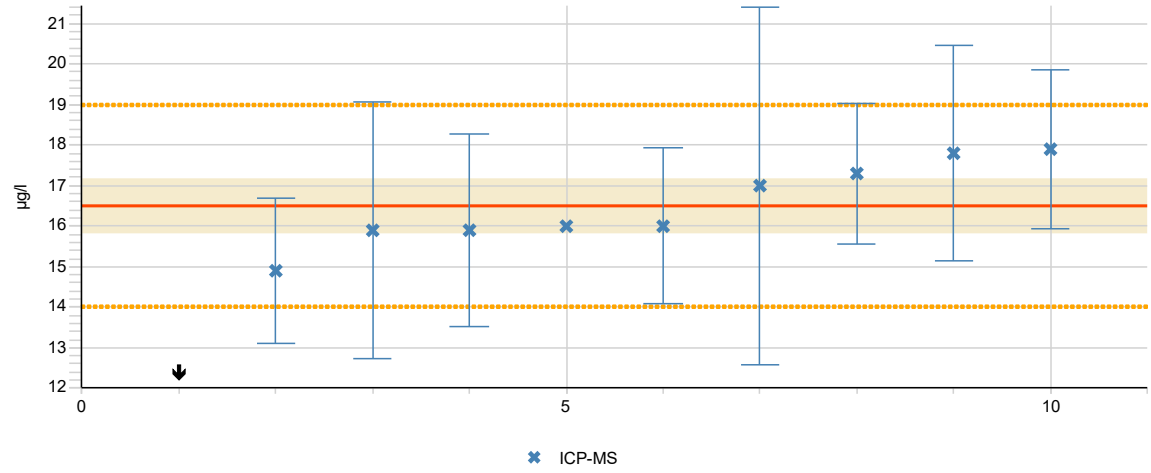
Measurand Mn Sample N2M



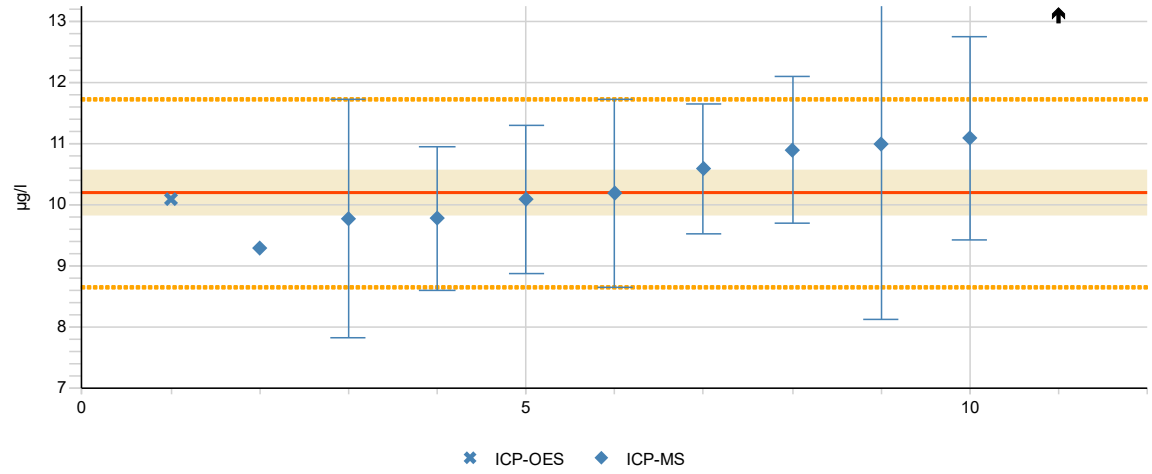

Measurand Mo Sample A1M



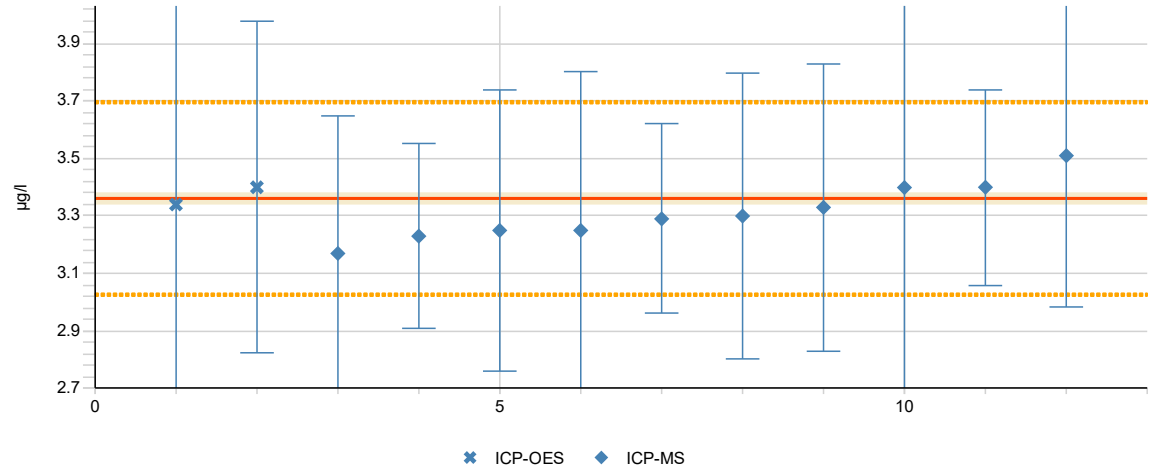

Measurand Mo Sample G3M



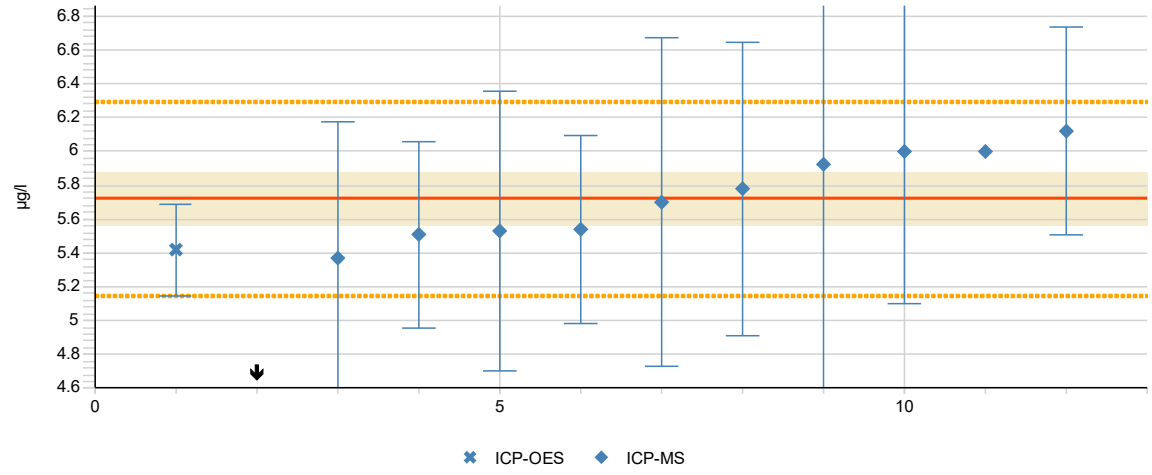
Measurand Mo Sample N2M



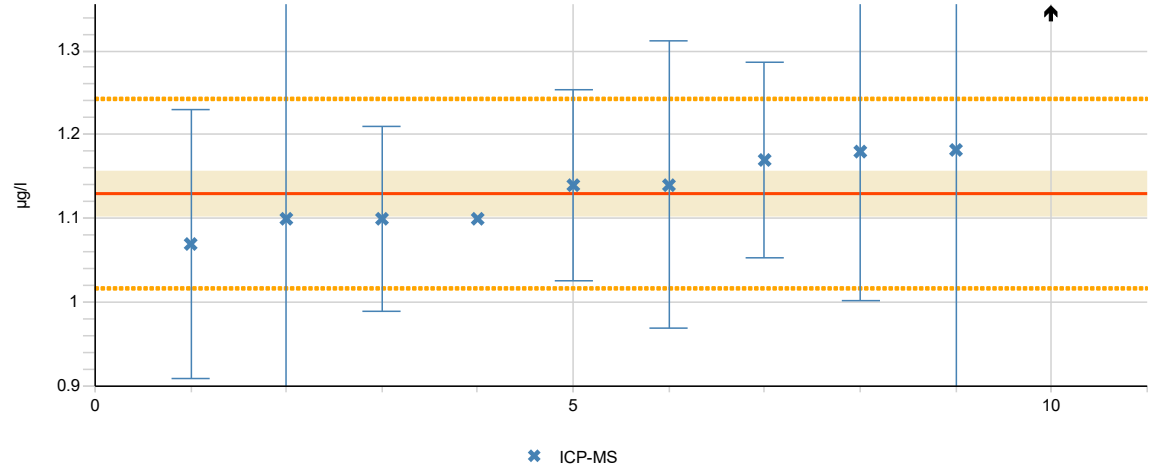

Measurand Ni Sample A1M



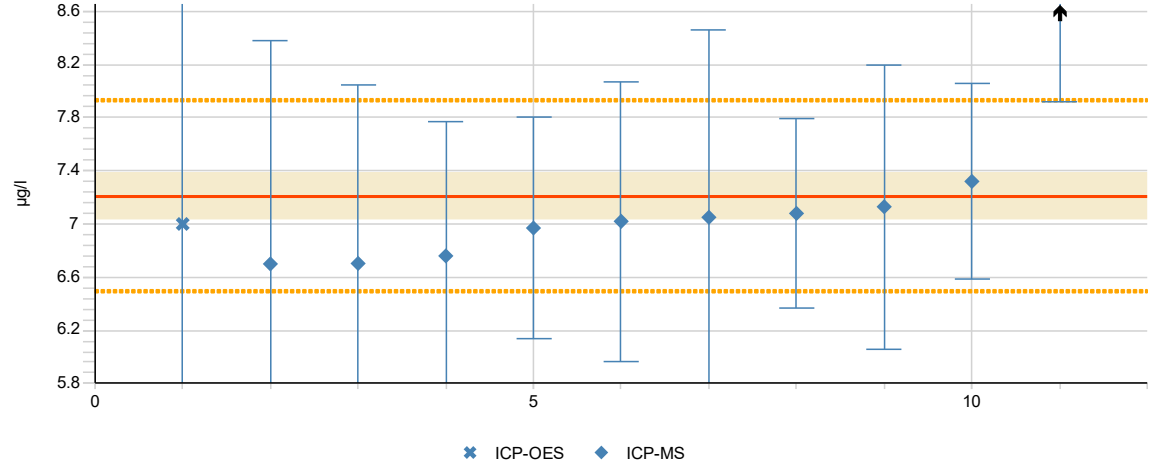

Measurand Ni Sample G3M



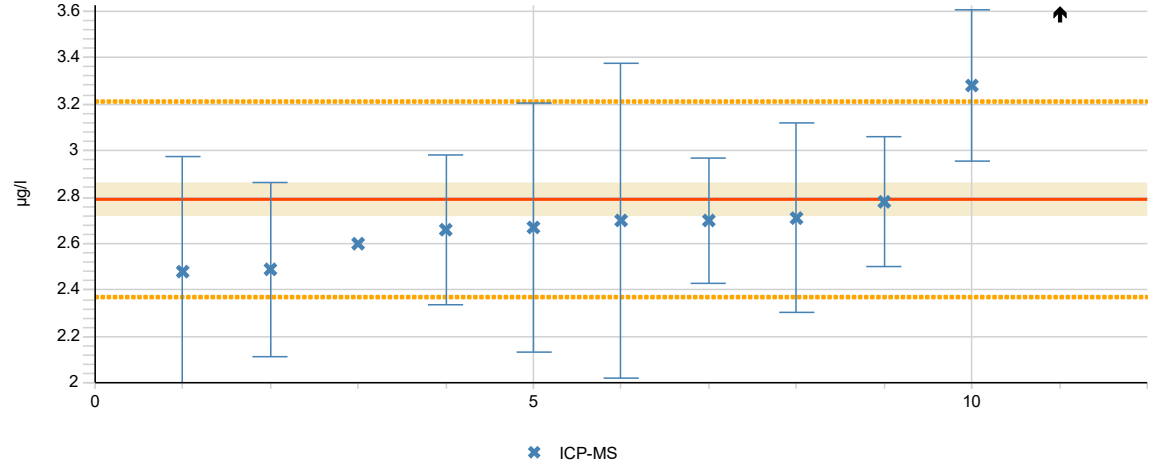
Measurand Ni Sample N2M



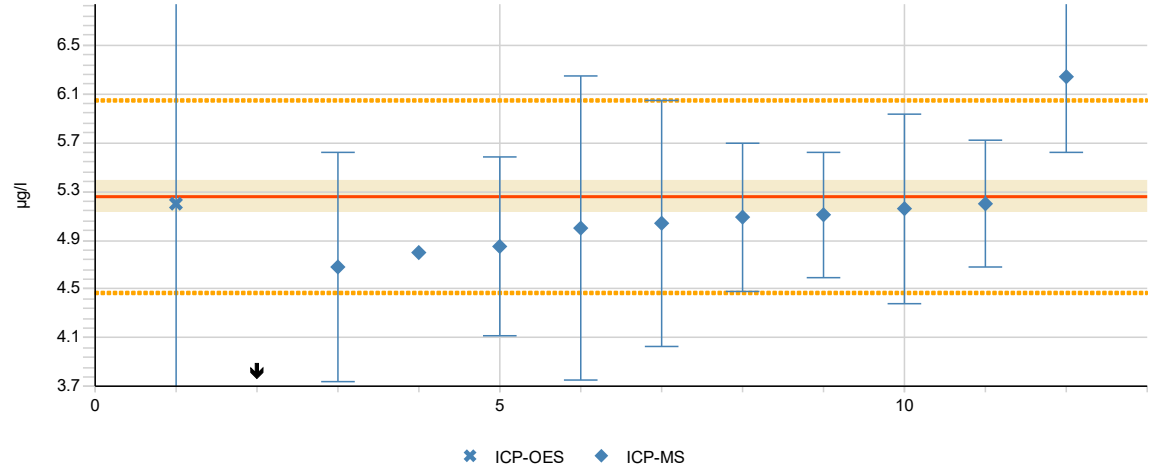

Measurand Pb Sample A1M



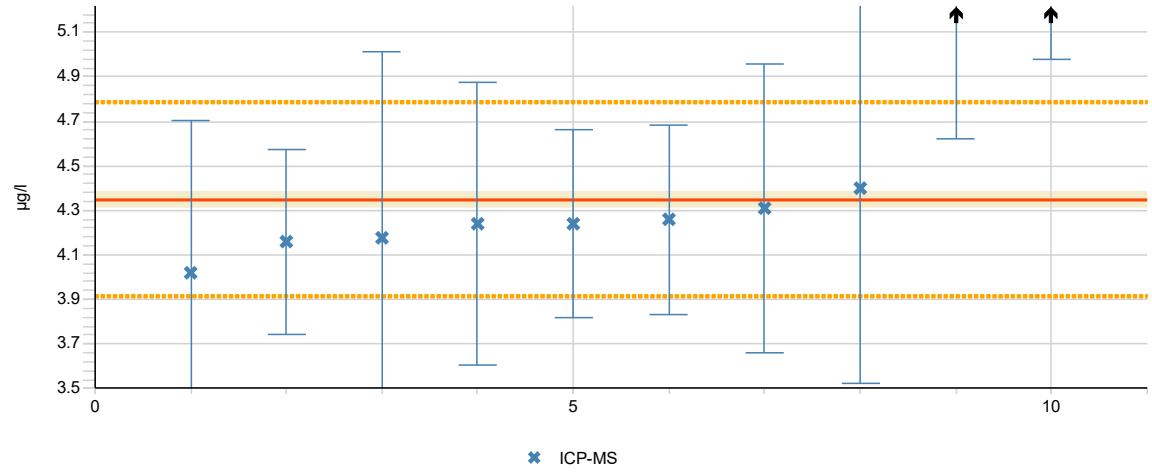

Measurand Pb Sample G3M



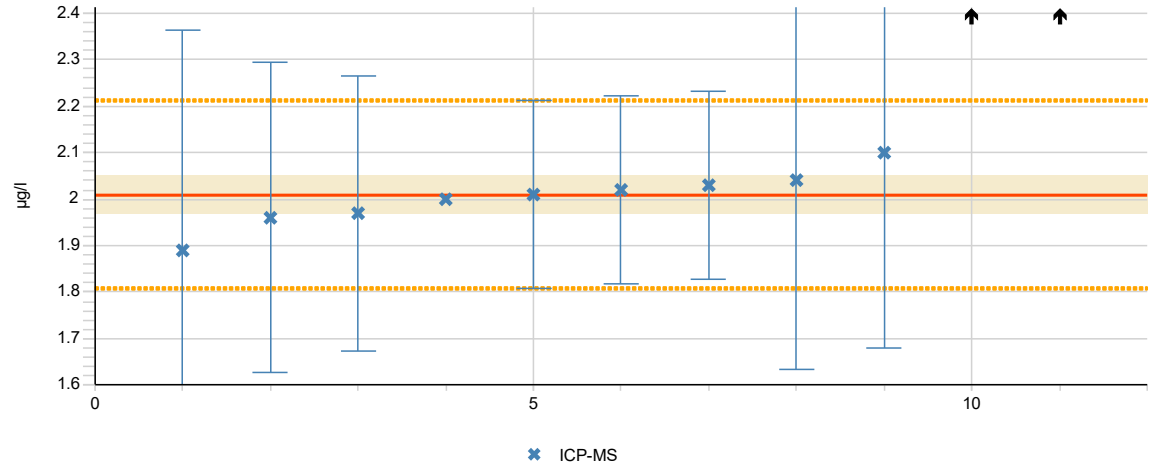
Measurand Pb Sample N2M



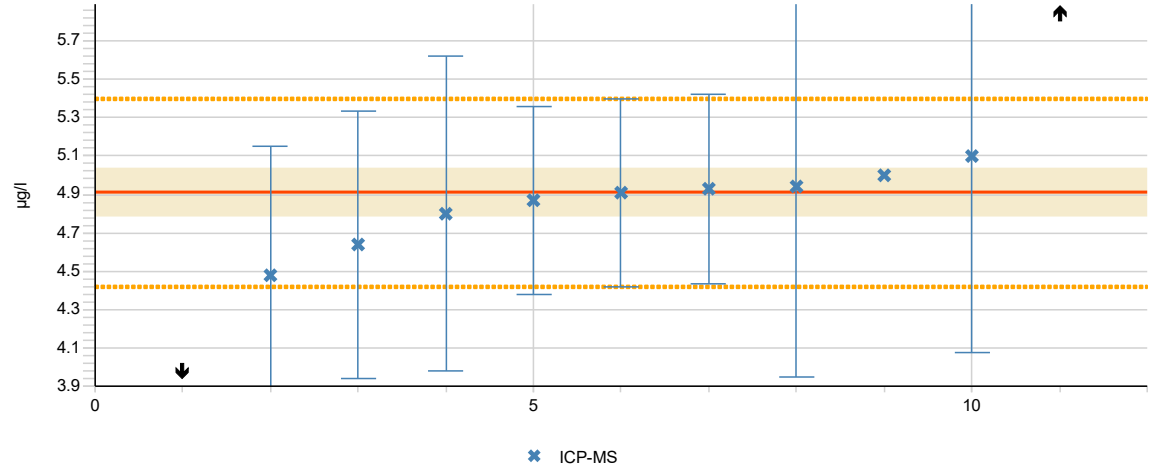

Measurand Sb Sample A1M



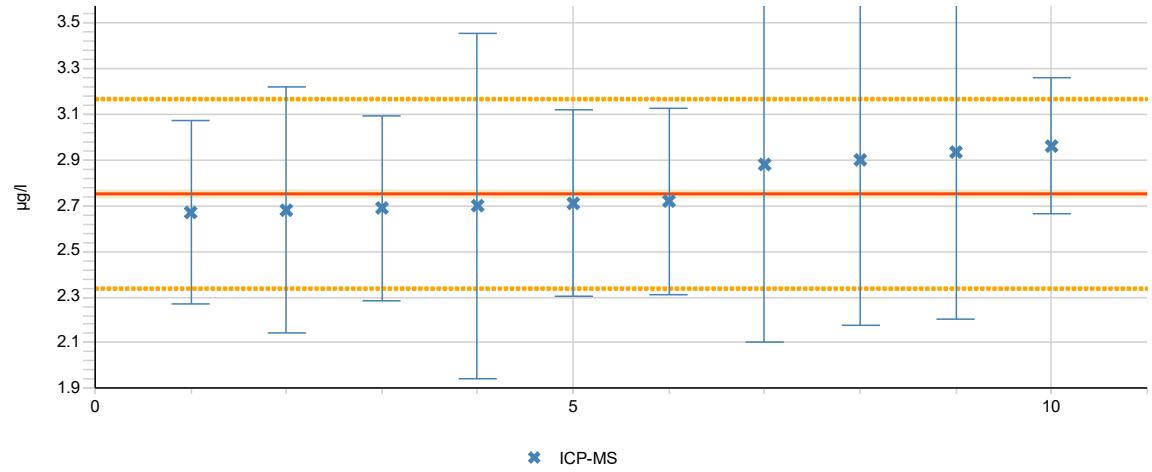

Measurand Sb Sample G3M



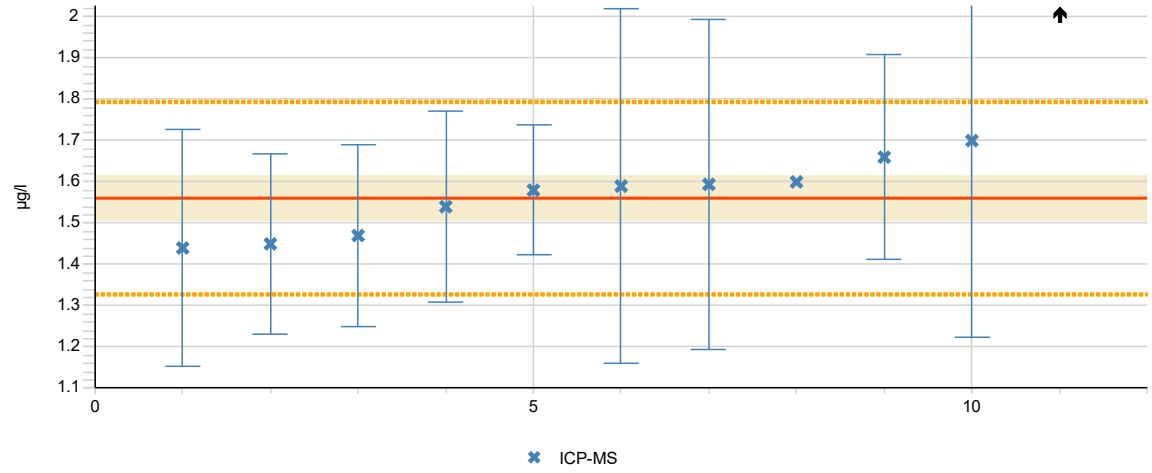
Measurand Sb Sample N2M



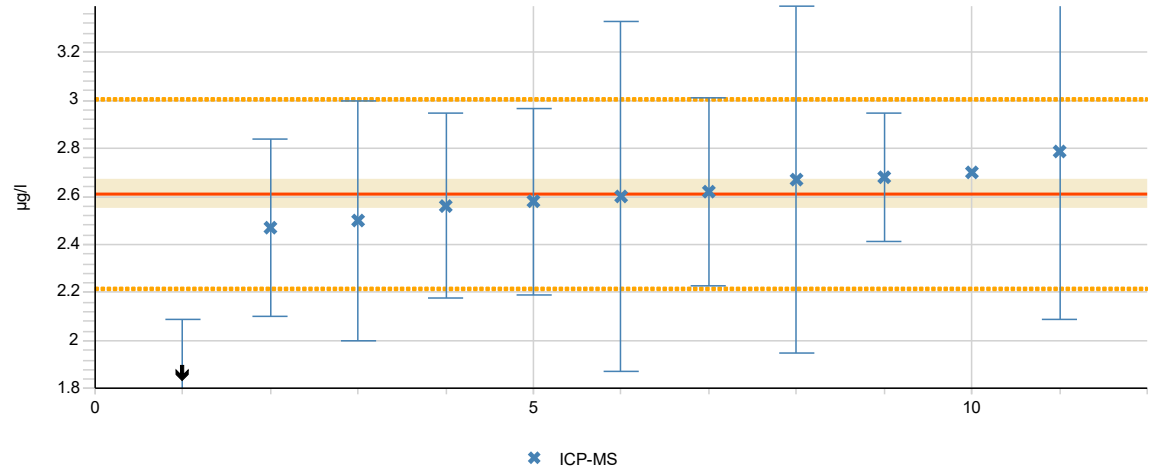

Measurand Se Sample A1M



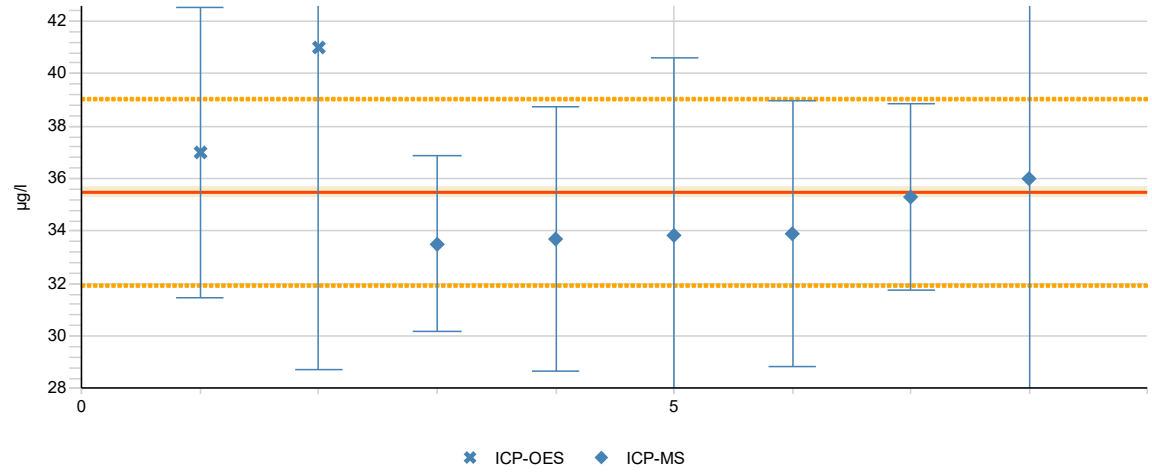

Measurand Se Sample G3M



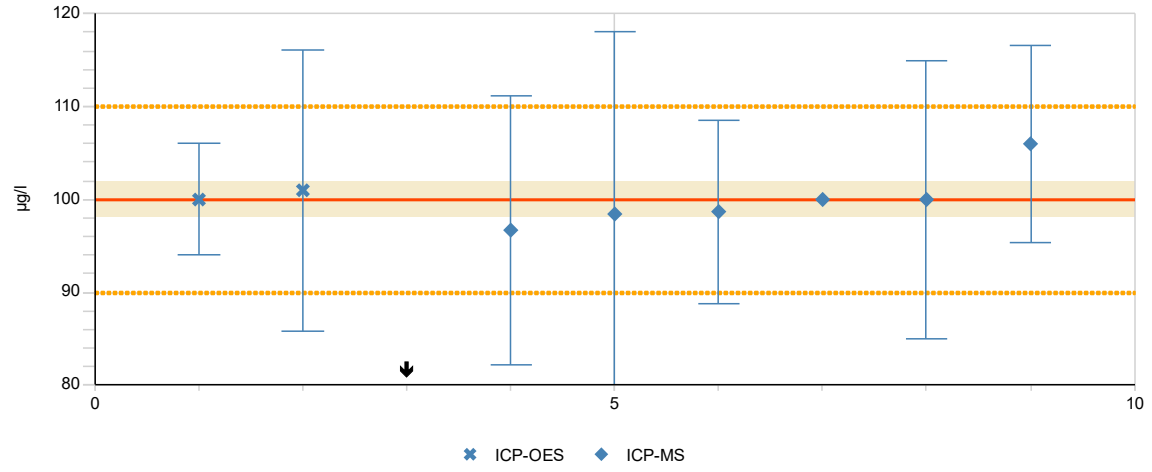
Measurand Se Sample N2M



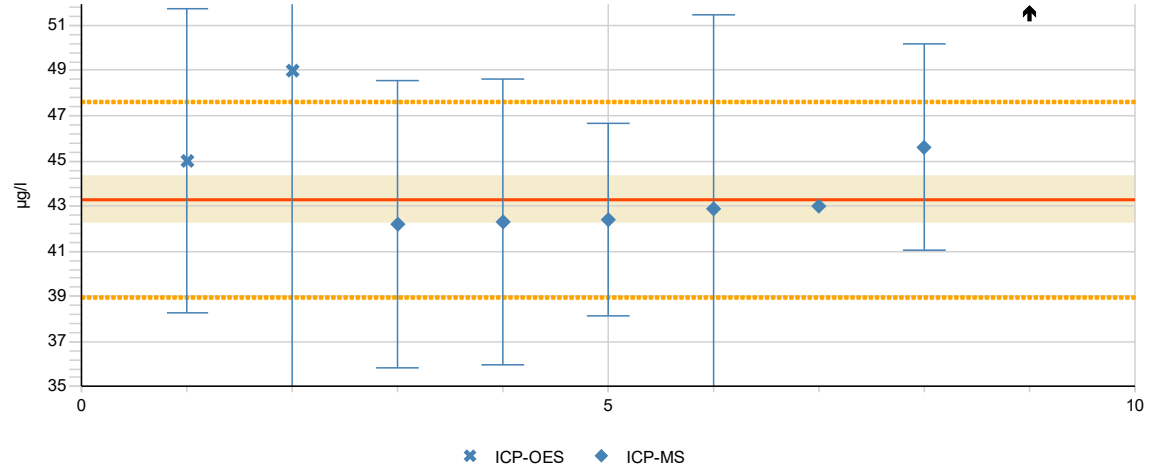

Measurand Sr Sample A1M



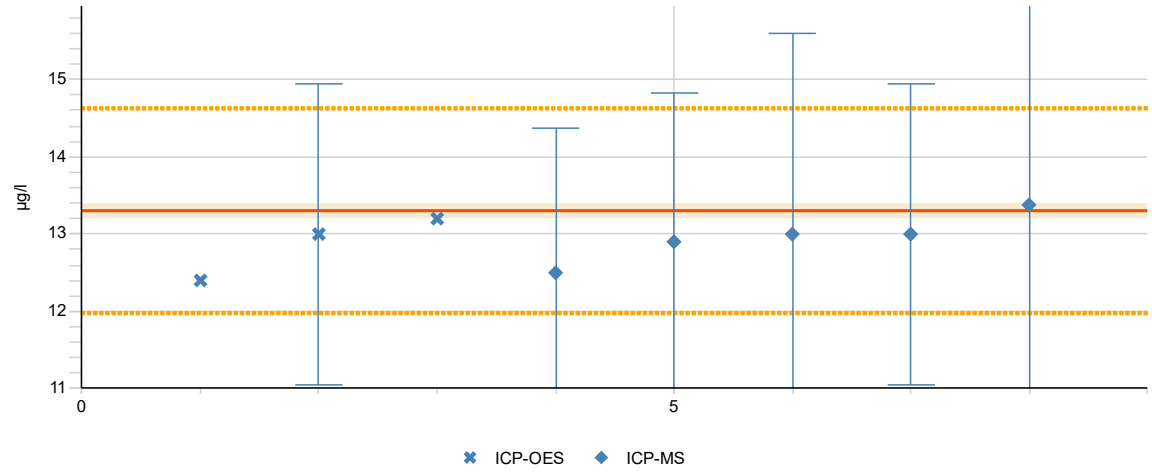

Measurand Sr Sample G3M



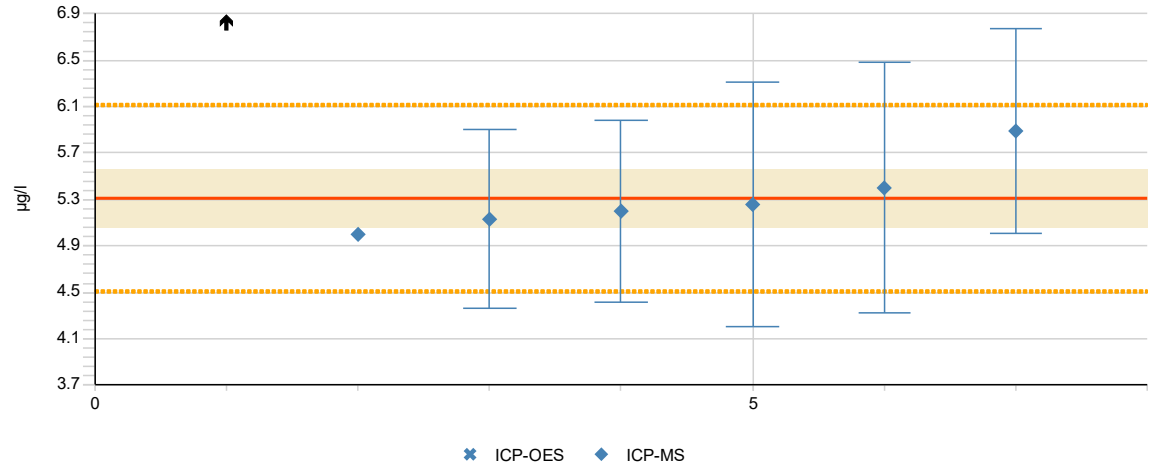
Measurand Sr Sample N2M



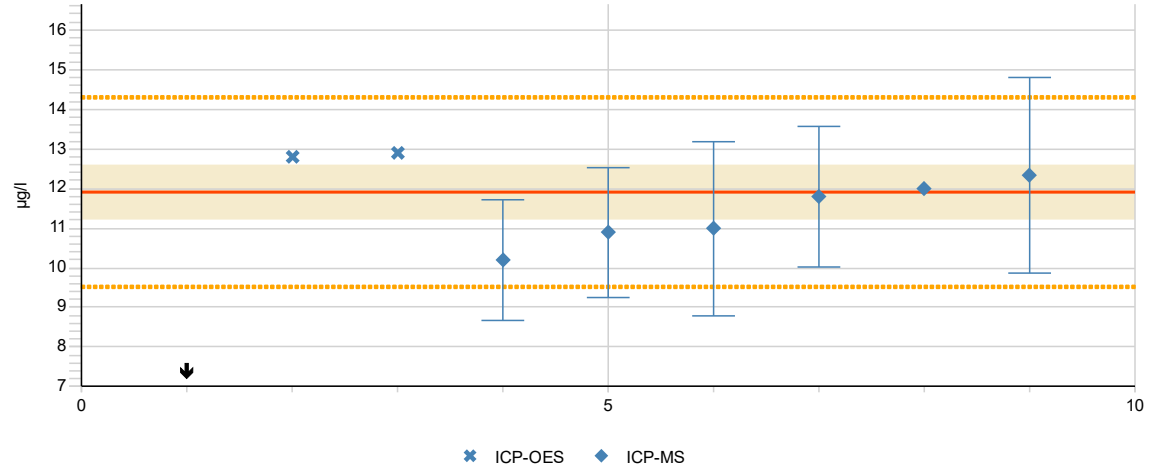

Measurand Ti Sample A1M



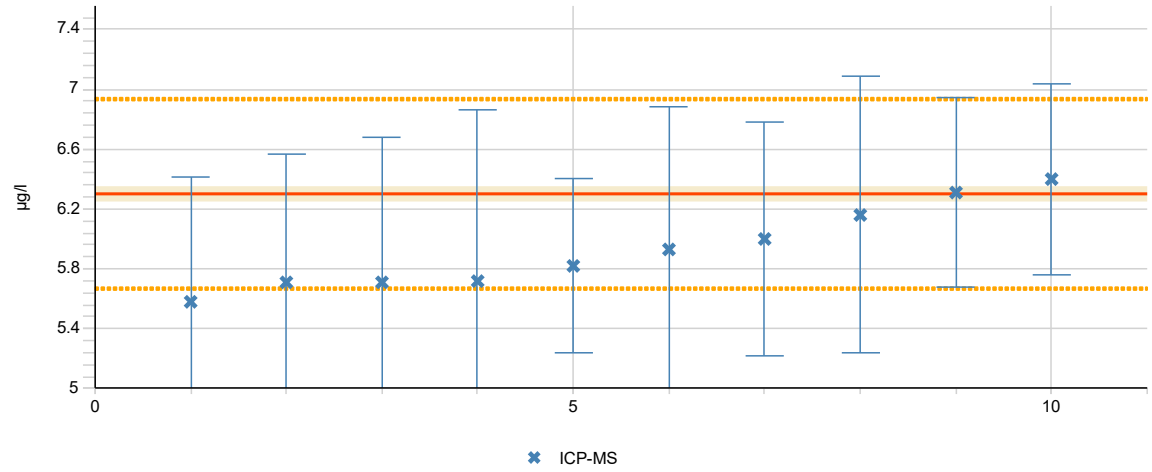

Measurand Ti Sample G3M



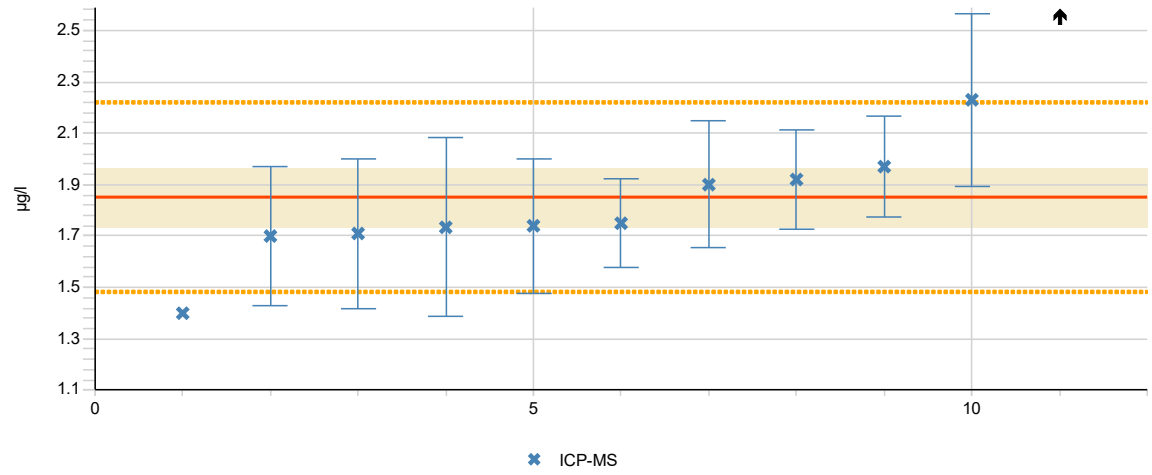
Measurand Ti Sample N2M



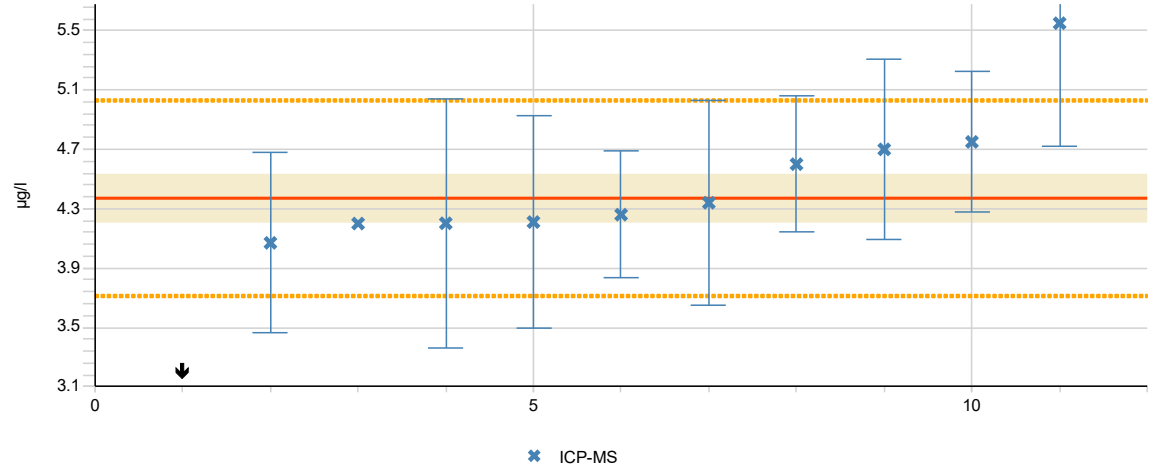

Measurand U Sample A1M



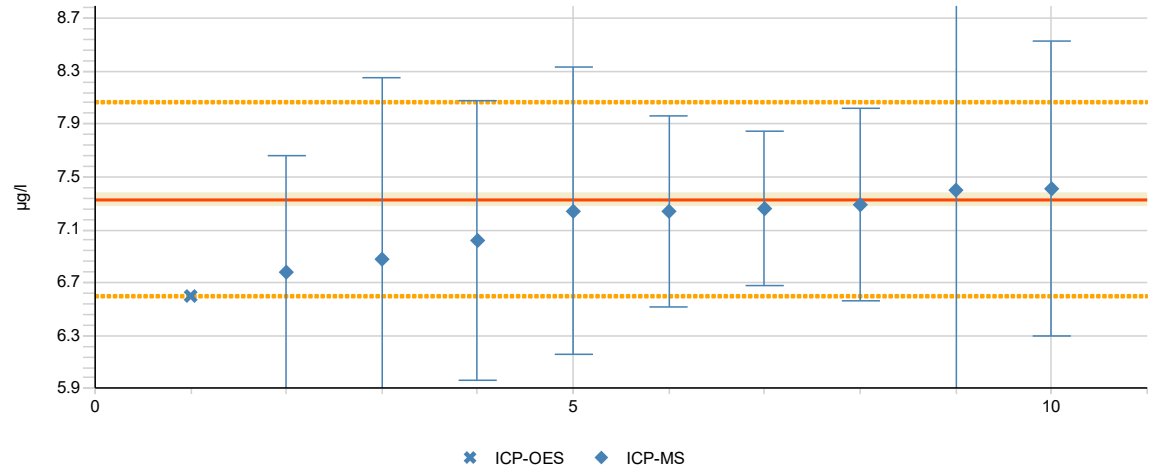

Measurand U Sample G3M



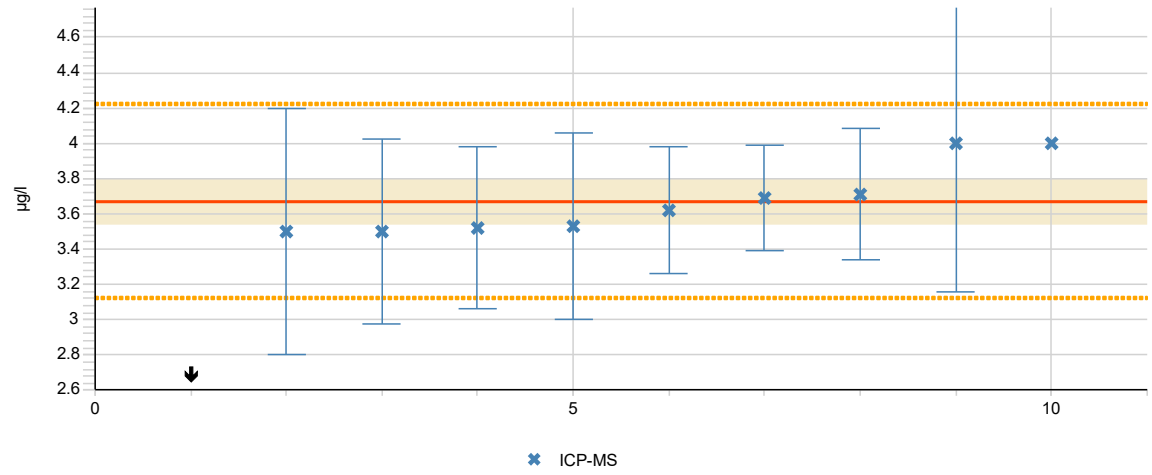
Measurand U Sample N2M



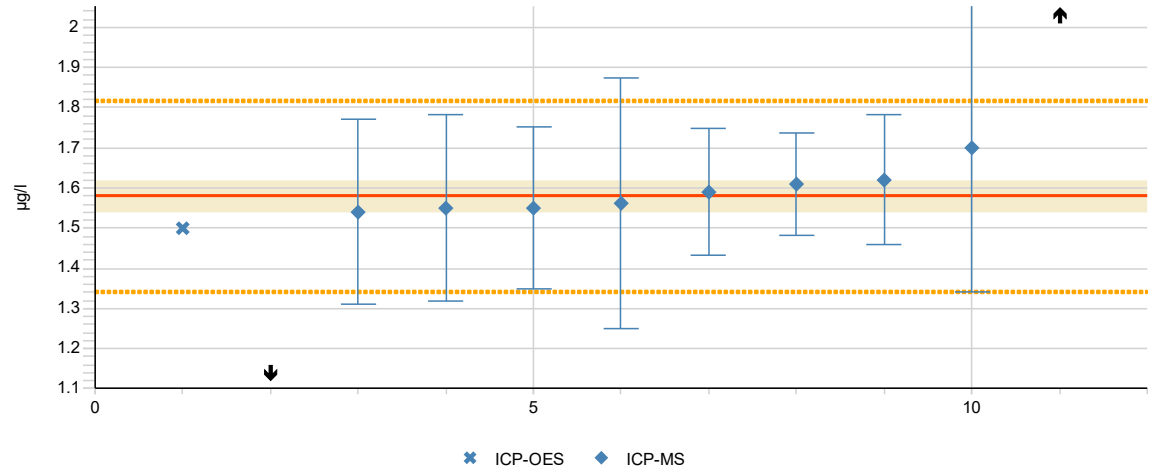

Measurand V Sample A1M



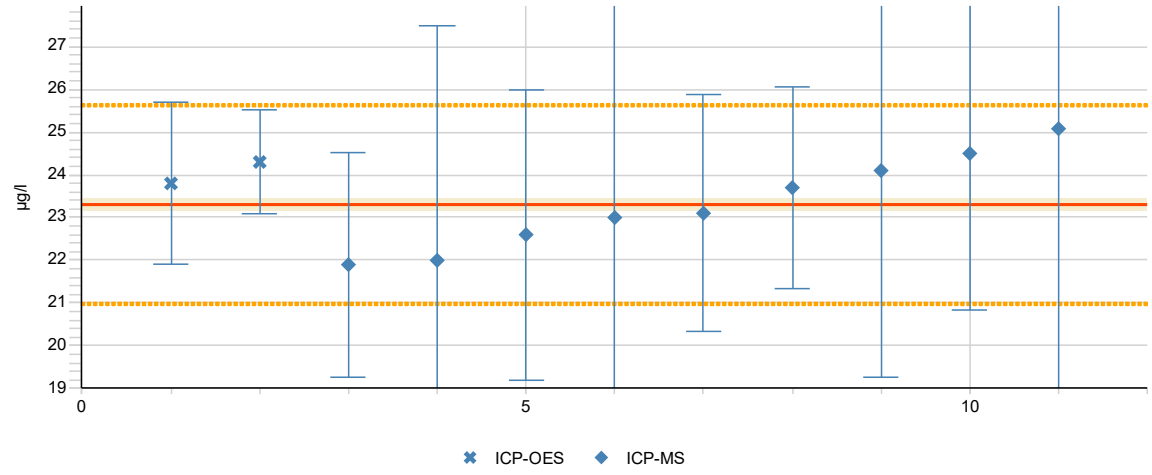

Measurand V Sample G3M



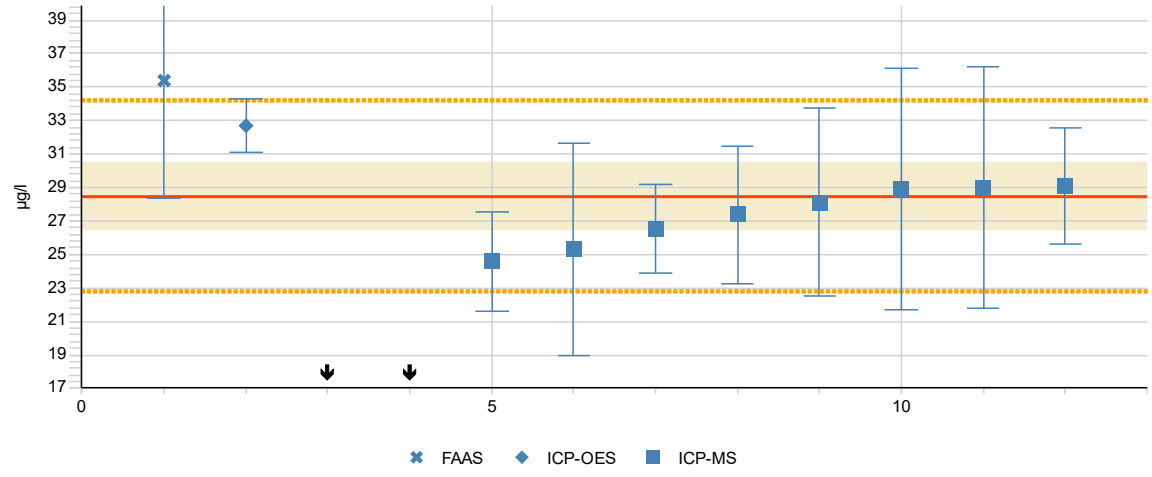
Measurand V Sample N2M

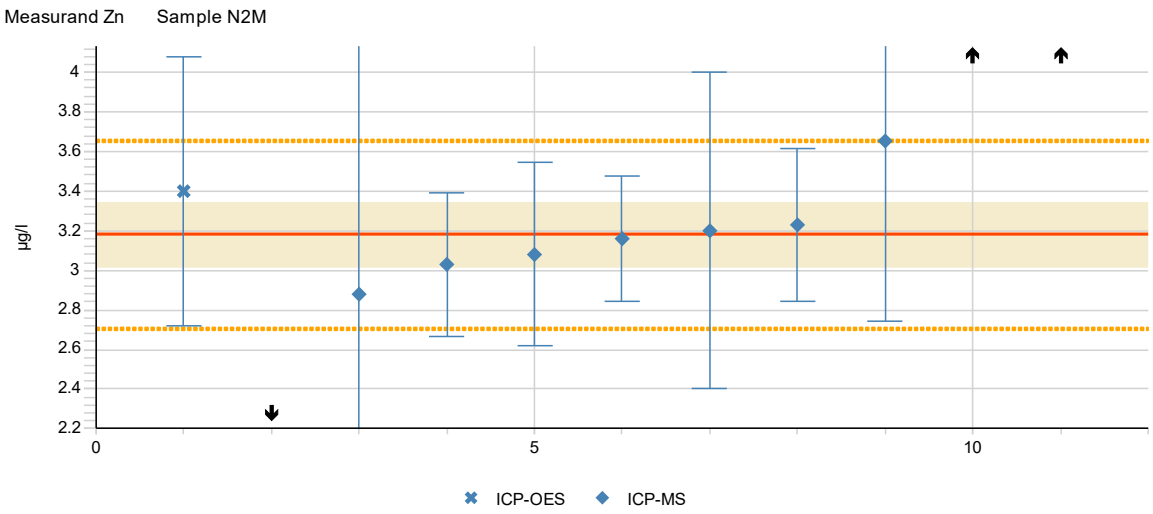



Measurand Zn Sample A1M



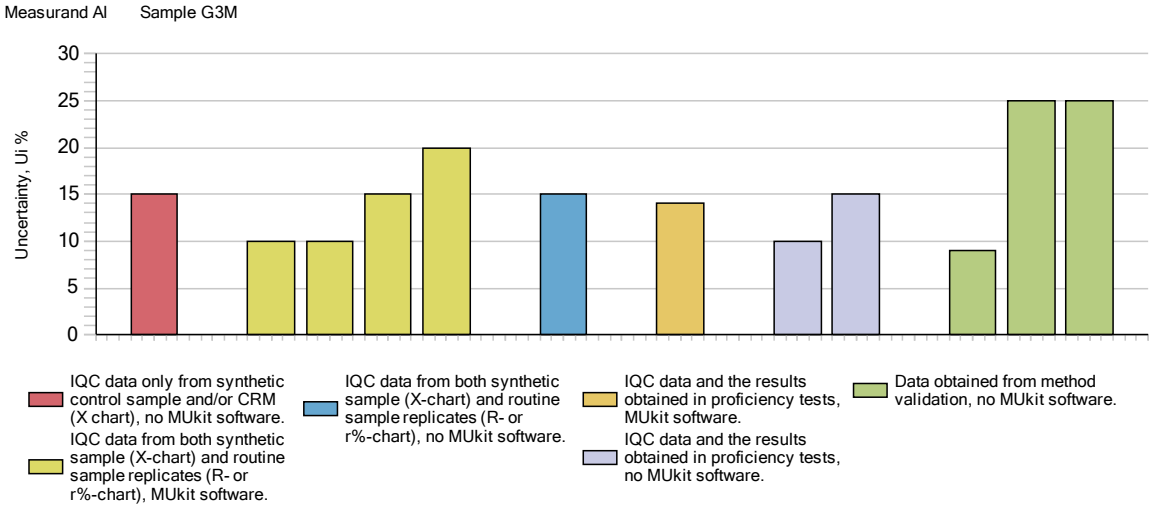

Measurand Zn Sample G3M

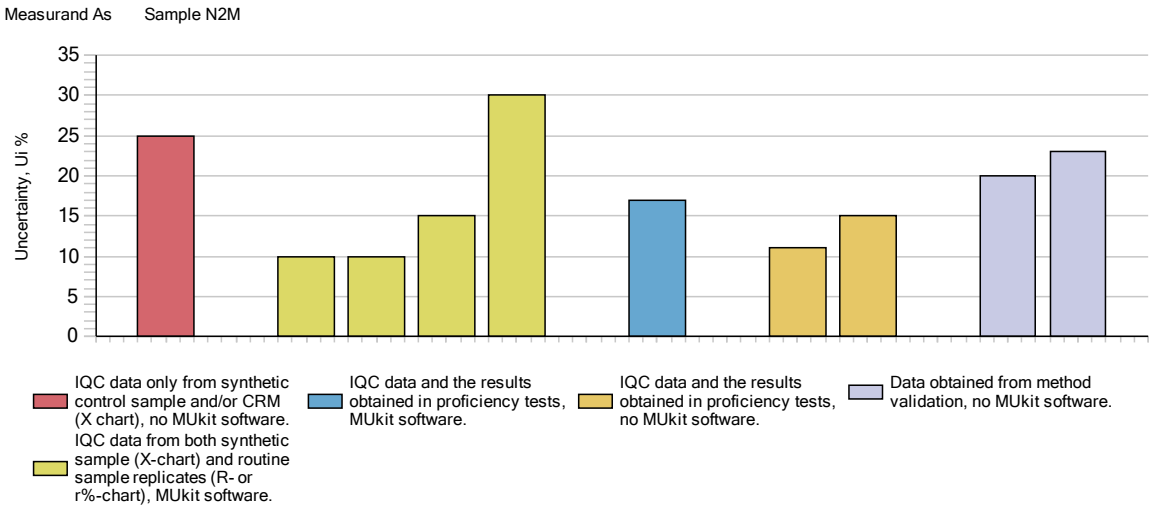



Measurand Zn
Sample N2M
µg/l
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
0
5
10
ICP-OES
ICP-MS

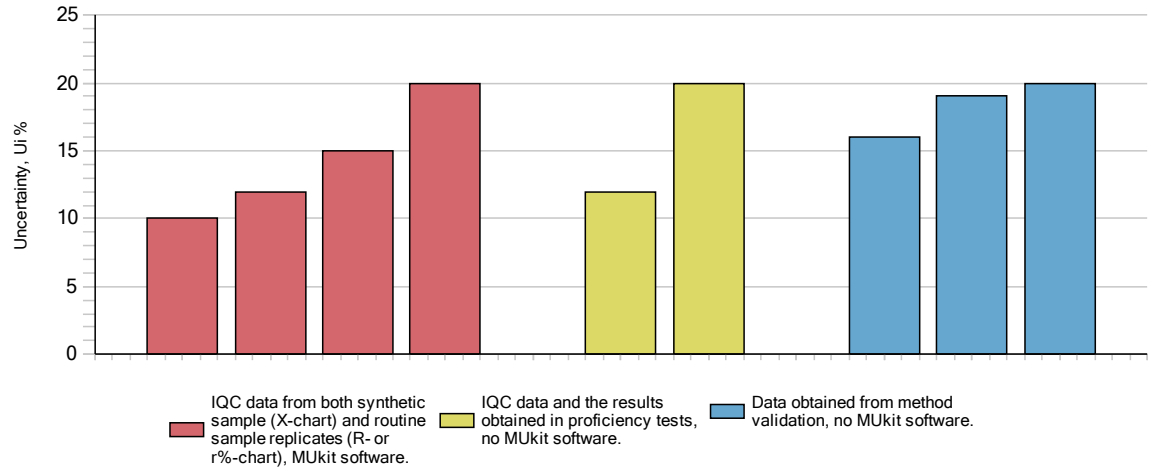
# APPENDIX 11: Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level ($k$=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [6, 7].

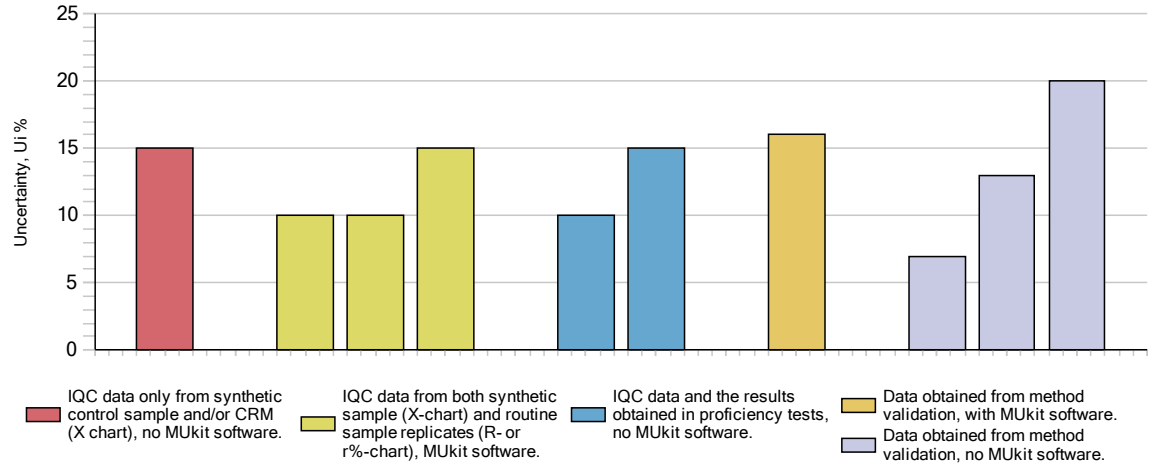


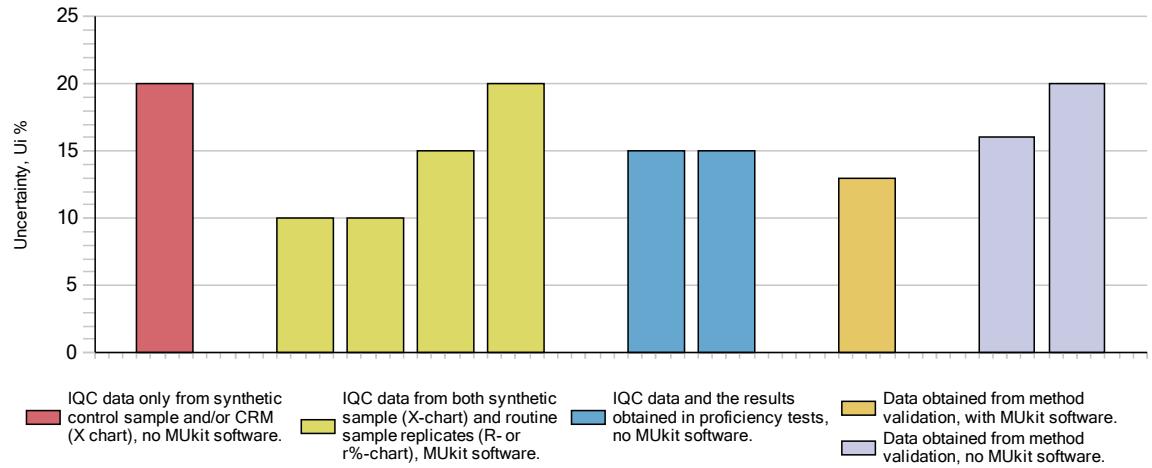
Measurand B Sample N2M



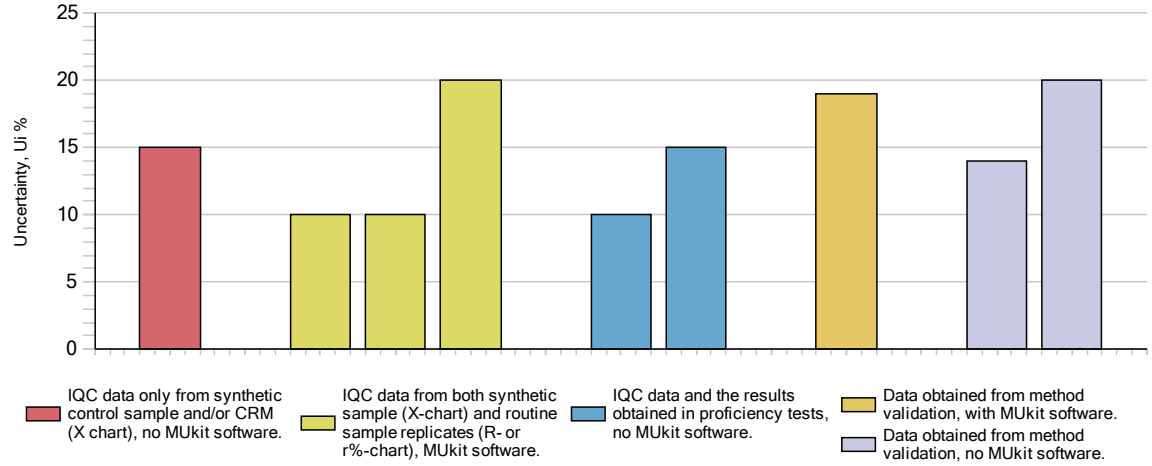

Measurand Ba Sample A1M



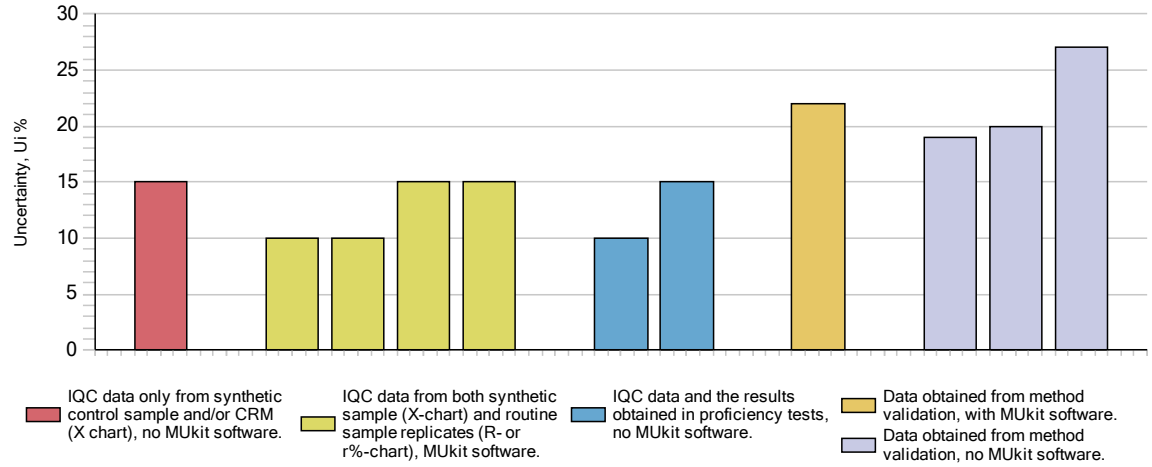

Measurand Cd Sample G3M



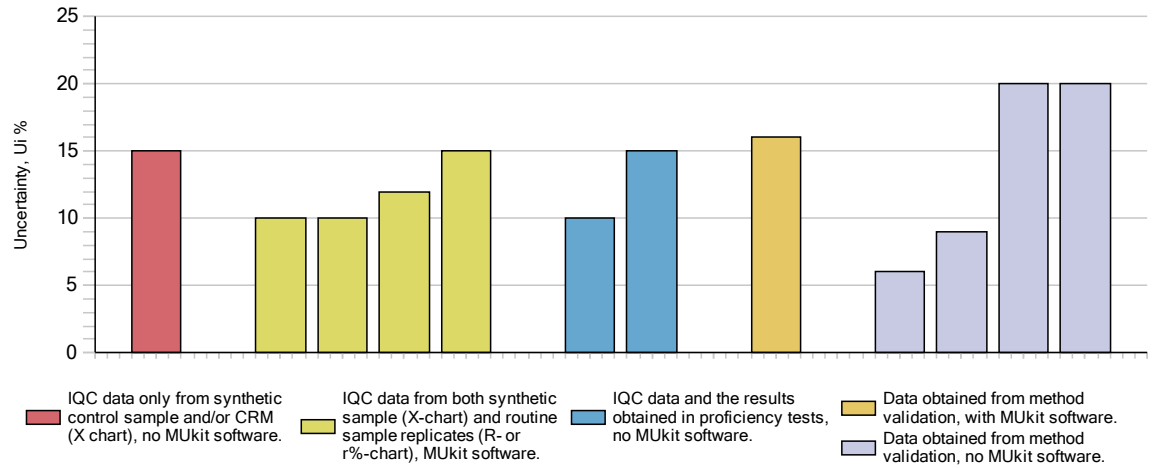
Measurand Co Sample G3M



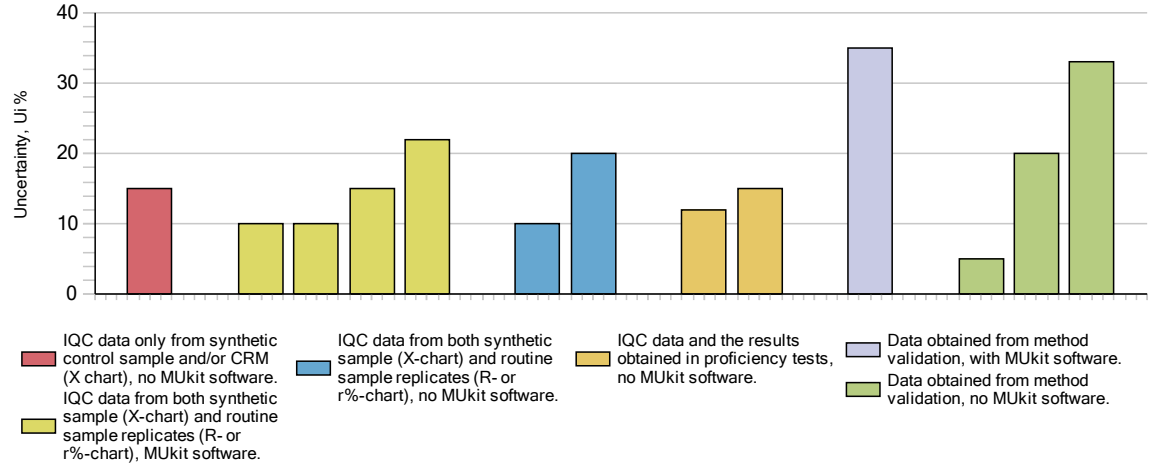

Measurand Cr Sample N2M



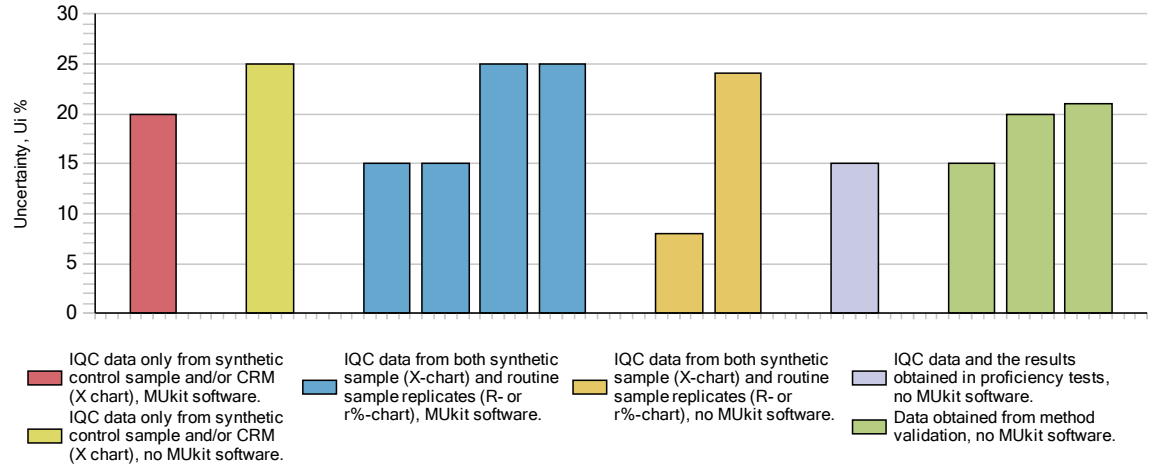

Measurand Cu Sample A1M



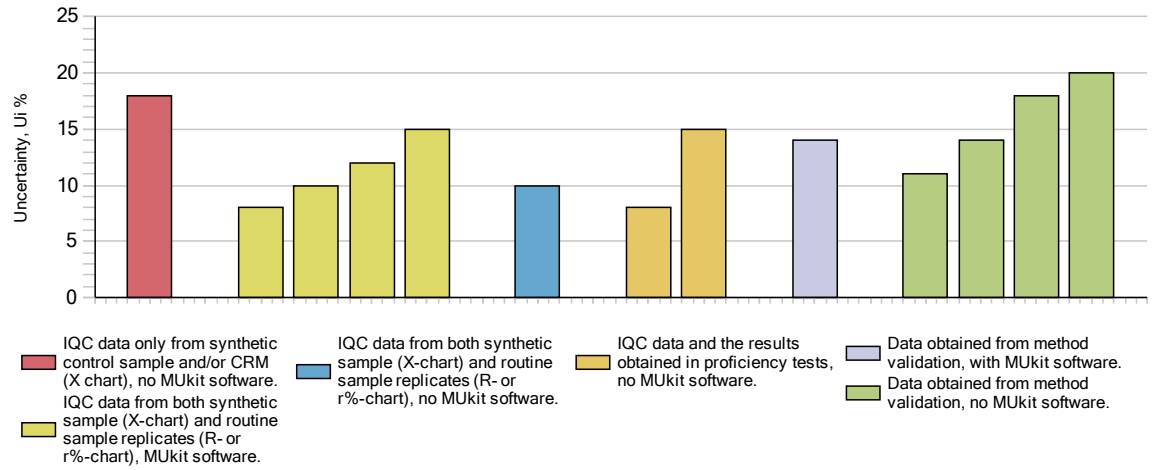
Measurand Fe Sample G3M



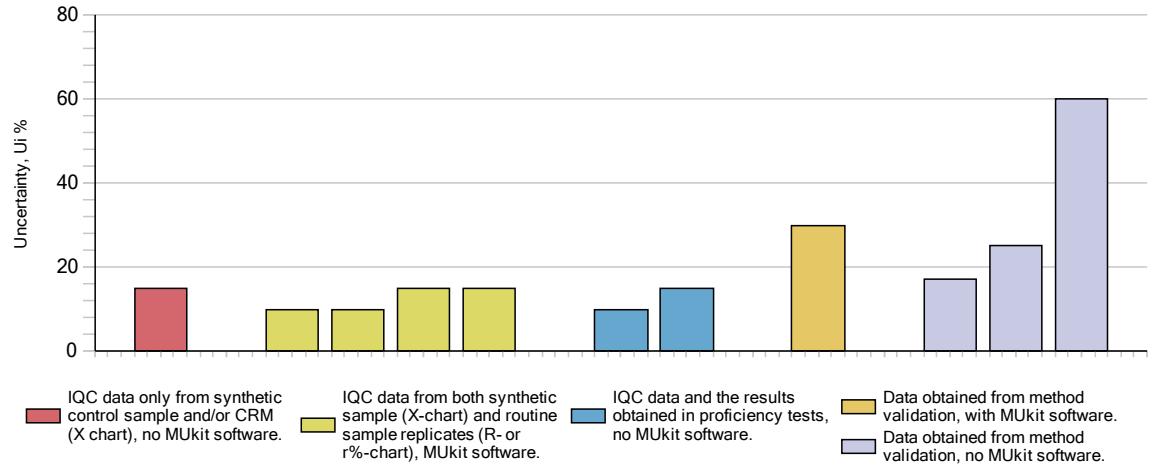

Measurand Hg Sample G3Hg



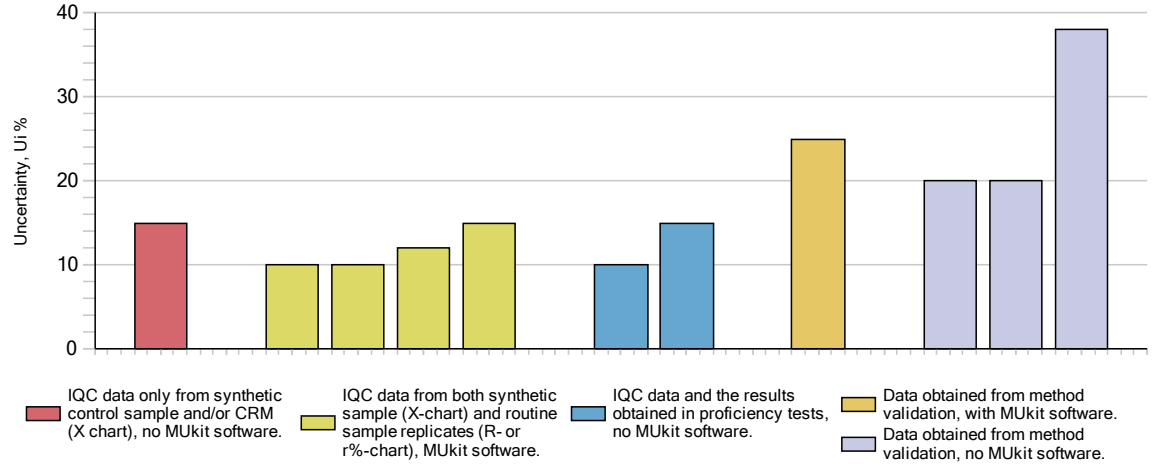

Measurand Mn Sample N2M



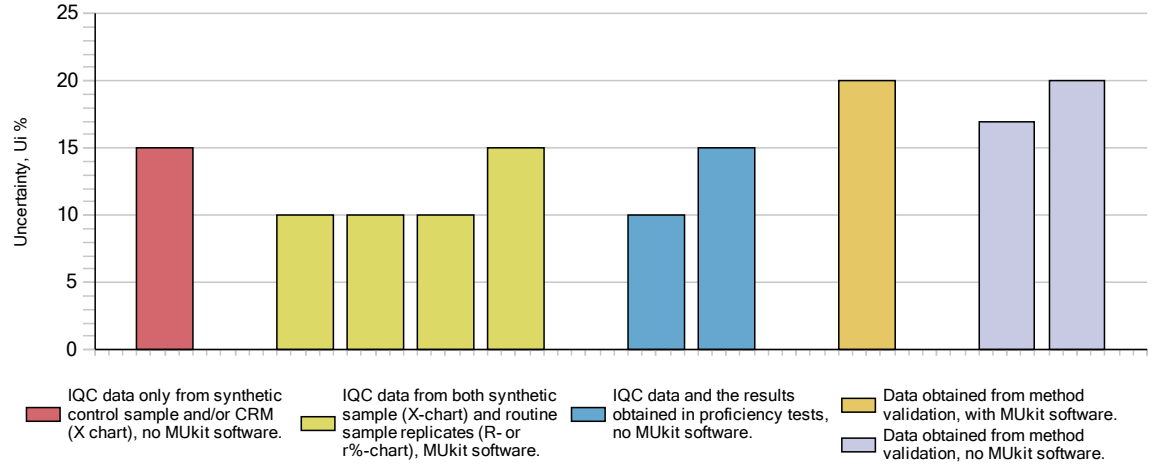
Measurand Ni Sample N2M

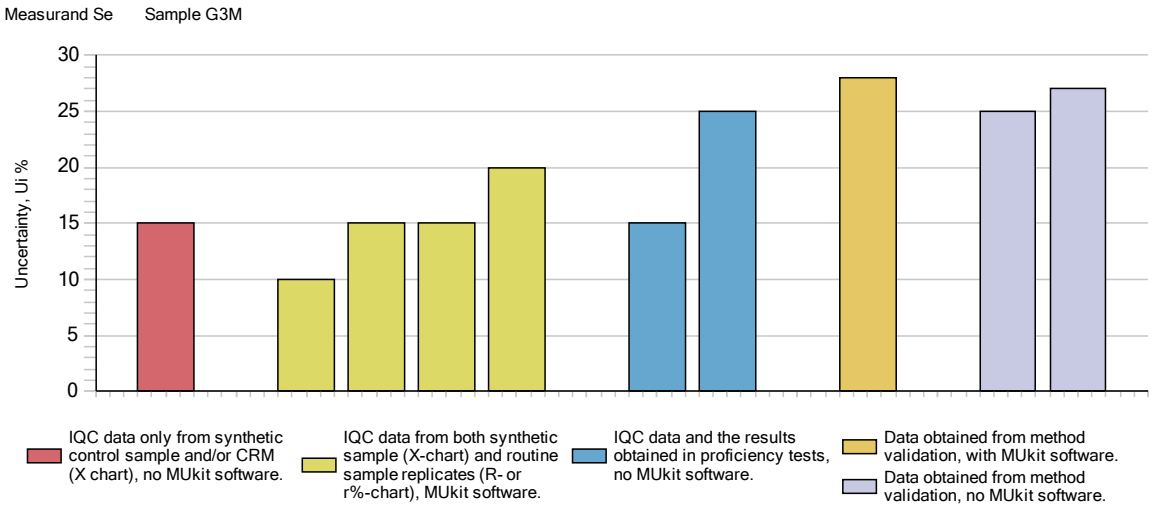


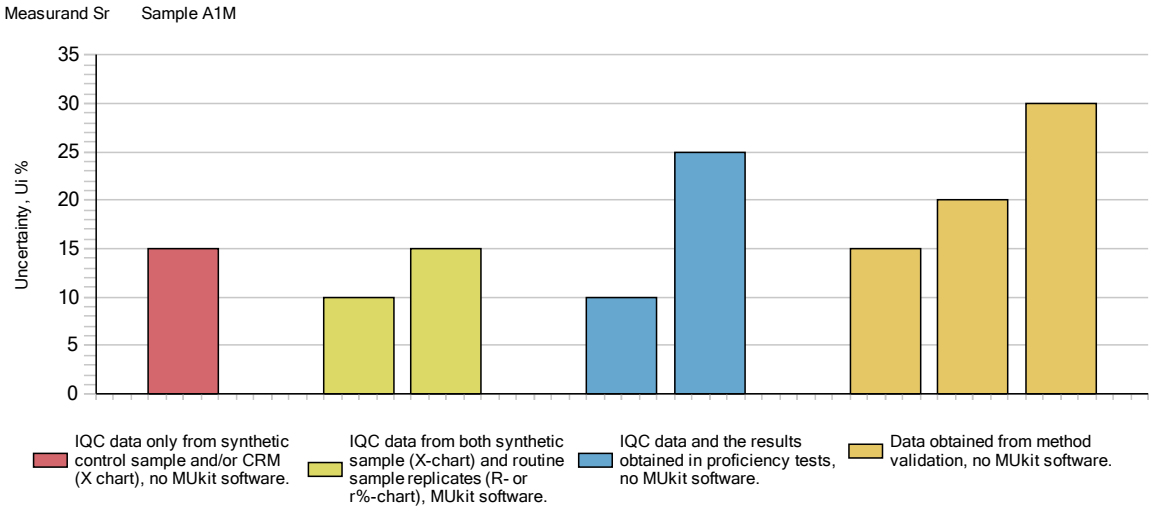

Measurand Pb Sample N2M

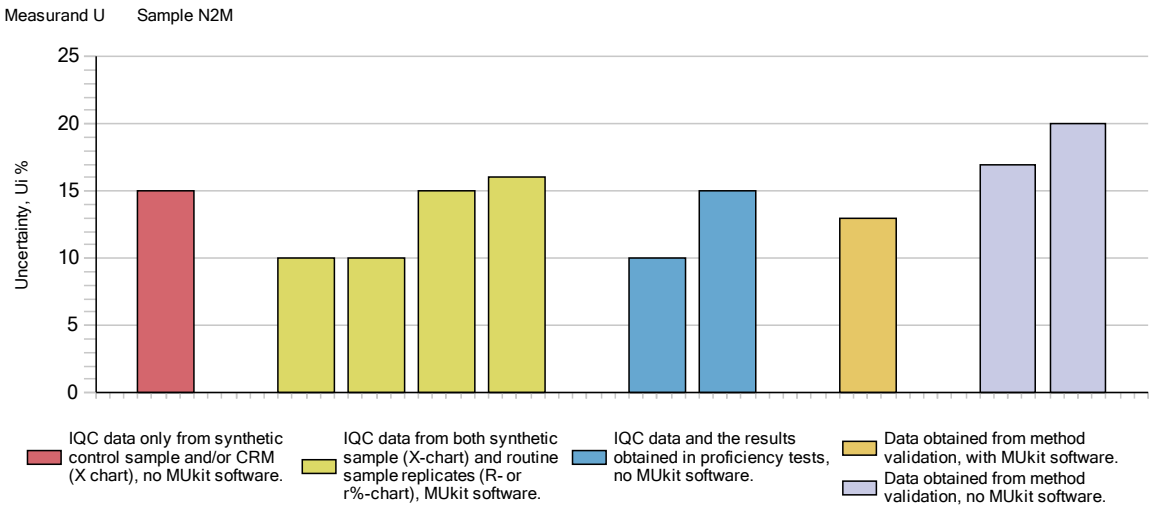



Measurand Sb Sample N2M

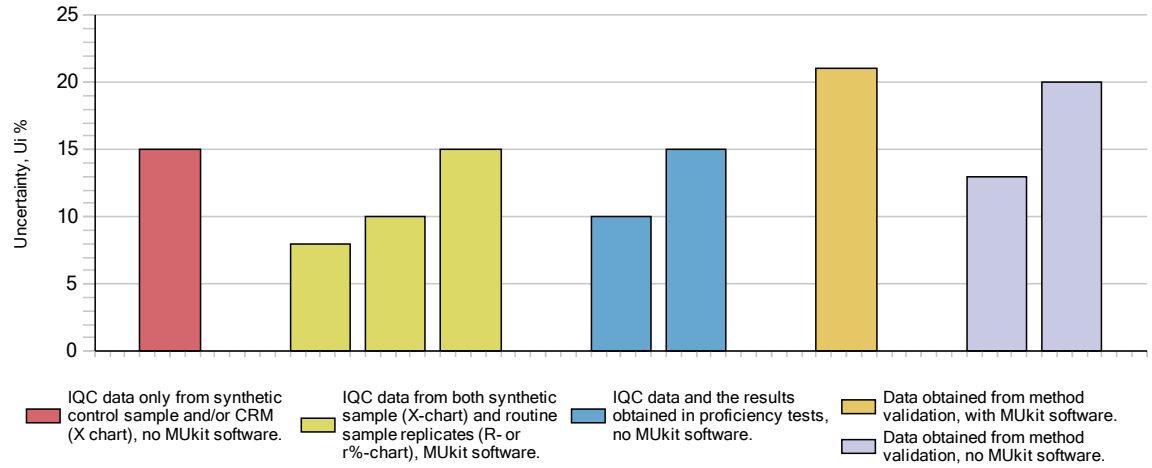



Measurand Se
Sample G3M
Uncertainty, Ui %
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

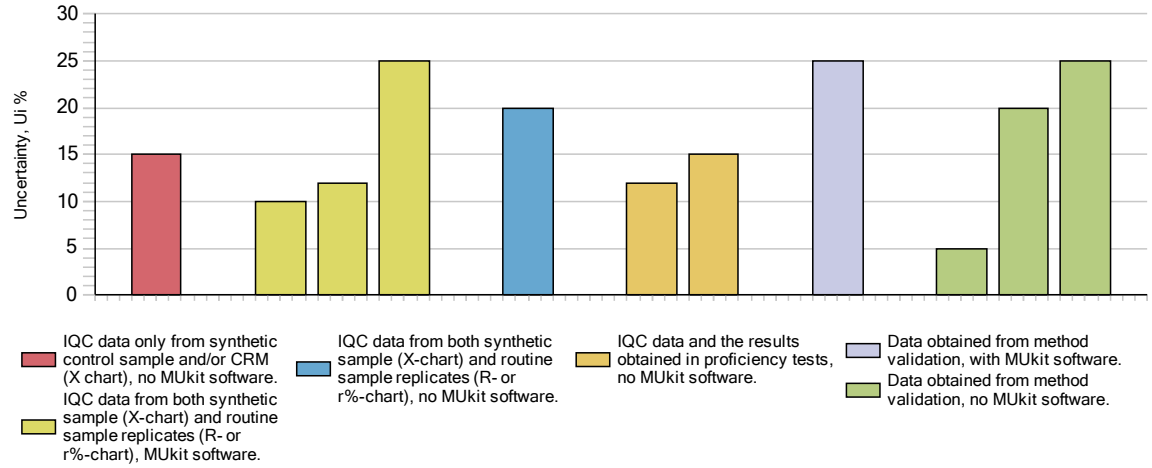

Measurand Sr
Sample A1M
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand U
Sample N2M
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

Measurand V Sample N2M




Measurand Zn Sample G3M



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